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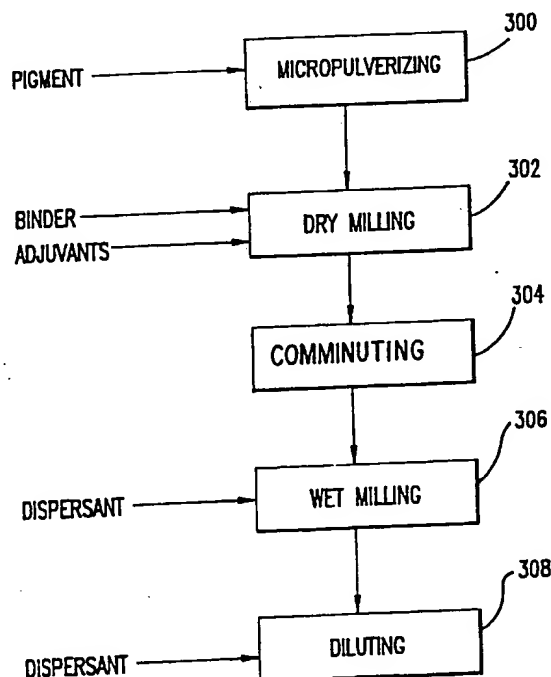
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(54) Title: ELECTROPHORETICALLY DEPOSITED PARTICLE COATINGS AND STRUCTURES MADE THEREFROM

(57) Abstract

This invention relates to a method of forming and using a very dense layer of particles that have been encapsulated in a thermoplastic polymer binder and electrically deposited on a substrate. Space-charge-limited deposition is made possible by the addition of novel charge directors that are essentially nonconductive in aliphatic hydrocarbon liquid in the absence of binder. The particle layer can be designed to possess numerous characteristics by varying the particles to be encapsulated. Many structures can be fabricated from the different particle layers including thermal detectors, electrical interconnects, p-n junctions, micro-metallic structures, field-emitting devices, and optical coatings. A technique for the removal of semiconductor dislocations is also discussed.



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**ELECTROPHORETICALLY DEPOSITED PARTICLE
COATINGS AND STRUCTURES MADE THEREFROM**

This is a continuation-in-part of copending application U.S. Serial No. 877,437, filed on June 2, 1986, which is a continuation-in-part of U.S. Serial No. 822,833, filed January 27, 1986, now U.S. Patent No. 4,719,026, which is a divisional of U.S. Serial No. 710,586, filed March 11, 1985, now U.S. Patent No. 4,585,535.

BACKGROUND OF THE INVENTION

Electrophoresis can be defined as the movement of colloidal ions as a result of an applied electric potential. Colloidal ions are ions that are larger than atomic or molecular dimensions but sufficiently small to exhibit Brownian movement when suspended in a medium. The electrophoretic deposition of a thin film of charged particles is well known and is the basis for modern xerography. In xerography, an image is projected onto a photosensitive drum to form a charged, non-visible image. The drum is then placed in contact with oppositely charged, pigmented particles. By electrophoresis, the pigmented particles move to the non-visible charged image, thereby forming a visible image of pigmented particles on the photosensitive drum. The visible image is then transferred from the drum to a carrier sheet by physical contact, electrostatic force, or other well-known methods. For electrophoresis to take place, the particles must

be suspended in a dispersant liquid and charged with a polarity opposite that of the substrate upon which they are to be deposited. The charging of the particles in the dispersant liquid is effected by charge directors. Since
5 the suspension must be nearly electrically neutral, charge directors not only introduce charges upon the particles to be deposited, but also introduce species having opposite signs called counter ions. The counter ions may be charged molecular ions, chain polymers, micelles, etc.
10 The charging of the suspension typically takes place by first allowing the charge director to disassociate into ionic species in the dispersant liquid. When the particles are added to the suspension, one ionic species preferentially attaches to the particles. The charge of
15 the ionic species that attach to the particles is usually a function of the surface properties of the particles and the ionic species comprising the charge director -- it is well known that a given charge director may charge one type of particle positively, another negatively, and a
20 third not at all.

When there are few charge-director ions attached per particle, the suspension is said to be "under-charge-directed" and there is a tendency for the particles to form floccules. Flocculation occurs because a neutral
25 particle adjacent to a charged one will experience an induced dipole that results in an attractive force, causing the particles to bind together. Flocculation is usually an unacceptable condition, and to prevent its occurrence, more charge director is added. However, if
30 excessive charge director is added, extra ions will be in the suspension with the same charge as the particles and the suspension is said to be "over-charge-directed". In such cases, the particles are electrophoretically deposited out of suspension under a condition known as
35 continuous phase conductivity. The extra or "free" ions of the charge director deposit out of solution before the pigment particles because these ions are much smaller and

mobile than the pigment particles. The free ions, however, contribute nothing to the particle layer and actually repel the later arriving pigment particles since the ions have the same electrostatic charge as the pigment
5 particles. Continuous phase conductivity thus reduces the density of the layer of particles electrophoretically deposited onto the substrate to below the optimum, theoretical level.

It is well known that the density, thickness and
10 other properties of a layer of particles deposited electrophoretically is a function of the average size, the standard deviation of the size and the composition of the particles being deposited. Large particles, having proportionately larger interstitial spaces between them,
15 produce layers having reduced density. Similarly, diversity in the size of particles causes proportionately larger interstitial spaces between the particles which also reduces the density of the electrophoretically deposited layer. It also known that particles which
20 chemically or electrically interact with the dispersant liquid, cannot be electrophoretically deposited to form a dense, uniform layer of particles.

Prior to electrophoretic deposition, all of the charged particles reach the same equilibrium
25 electrochemical potential in the suspension. At equilibrium, the charge on a given spherical particle is proportional to its radius. Similarly, the viscous drag on a spherical particle in a liquid is proportional to its radius. Therefore, the mobility, which is proportional to
30 the charge per particle and inversely proportional to the viscous drag, will tend to be independent of particle size. However, larger particles may also experience a dielectrophoretic force caused by an induced polarization interacting with an electric field gradient. This causes
35 the larger particles to deposit first. In other words, particles with different sizes will respond differently to an induced electrical field, which tends to produce non-

uniform deposits of particles. Therefore, the particle size distribution should be kept as narrow as possible.

The properties of a layer of electrophoretically deposited particles also depends on the average mobility
5 and the average charge per particle being deposited. The particle density, charge, and mobility of the counter ions are also important, as is proper solution maintenance to avoid "exhaustion" due to depletion.

However, even if all of the variables affecting the
10 uniformity of an electrophoretically deposited layer of particles are controlled, under-charge-direction and the resultant flocculation or over-charge-direction and the resultant continuous phase conductivity will serve to limit the density, uniformity and properties obtainable
15 from a particle layer formed by prior art methods of electrophoretic deposition.

In copending U.S. Serial No. 877,437, incorporated herein by reference, preparation and use of a copper particle layer which exhibits properties useful in the
20 fabrication of thermal detectors is disclosed. The layers of copper particles disclosed in Serial No. 877,437 were made by encapsulating copper particles in a charge-directed thermoplastic resin. This resin is insoluble in the liquid dispersant into which the encapsulated copper
25 particles are suspended. The resulting suspension, i.e., the resin-encapsulated copper particles in dispersant, is then electrophoretically deposited onto an appropriate substrate. An analysis of these films showed that they were different from such films deposited by other
30 electrophoretic deposition techniques. For example, the layers were extremely uniform and the discrete encapsulated copper particles had diameters of approximately one micron. Moreover, the electrical properties did not vary appreciably across the entire area
35 of the layers or with the passing of time.

It has been determined that the particle layer disclosed in Serial No. 877,437 resulted from the

electrophoretic deposition of particles out of suspension under space-charge-limited-current conditions. Under this condition, the suspension of particles is neither under-charge-directed nor over-charge-directed, i.e., there are
5 no uncharged particles, but similarly, there are no free ions having the same charge as the particles. Since the charge on a given deposited particle repels other particles to adjacent areas where fewer charges have been deposited, the particles deposit uniformly out of
10 suspension once an electrical field is applied. In this way, the toner particles in suspension are uniformly transferred to the toner layer.

Space-charge-limited current electrophoretic deposition can be conceptualized as a suspension of
15 charged particles consisting of positive counter ions which are smaller and more mobile than the negatively charged toner particles to be deposited. When a suspension of charged particles located between two electrodes is subjected to a step voltage, the more mobile
20 positive counter ions respond first and accumulate or discharge at the negative electrode. This leaves a region adjacent to the positive electrode that is depleted of counter ions, known as a depletion or space-charge region. The thickness of this depletion region is influenced by
25 the counter ion density and the magnitude of the applied voltage. Just after the formation of the depletion region, the voltage drop in the suspension is essentially across this region. Therefore, this is the only region where a field is present to cause the slower toner
30 particles to migrate. Thus, the only particles that one expects to accumulate rapidly are those in this region. The deposition of the toner particles out of the transient depletion region of the suspension is believed to be an important factor contributing to the high particle density
35 achieved by our invention. If the deposition time is long compared to the time for the particles in the depletion region to reach the positive electrode, then additional

particles will be deposited out of the bath, but at a slower rate and a lower packing density, due to particle repulsion and a smaller field arising from a widening of the depletion layer.

5 For electrophoretic deposition to take place under optimum space-charge-limited current conditions, the suspension must not be over-charge-directed or under-charge-directed. Consequently, electrophoretic deposition under space-charge-limited current conditions is
10 facilitated by the use of novel charge directors which remain neutral in non-polar dispersant liquid until the particles to be deposited are added to the suspension. Once the particles are added, they become charged with one polarity and the remaining portion of charge director
15 molecules retains the opposite polarity. This charging is due to enthalpy differences between the charge director and the particles. Depending on the materials involved, the charging of the particles results from the exchange of electrons or ionic molecular groups between the particles
20 and the charge director molecules.

Steps for preparing a particle suspension that can be electrophoretically deposited under space-charge-limited current conditions to produce a film of thermosensitive copper particles are disclosed in Serial No. 877,437.
25 First, a two-roll rubber mill of a type known to the art is charged with various thermoplastic binders, copper particles and various addition agents. The thermoplastic binders comprise long carbon chains having various chemical groups which serve as functional sites, or
30 "hooks", with which the charge director may react. The copper particles, the binder, and the various addition agents are blended in a rubber mill at 130°C for about one hour, i.e., until the copper is uniformly dispersed.

Upon cooling, the resultant mixture (i.e., the binder
35 encapsulated copper particles) solidifies into a crayon-like mass, which is comminuted into a powder. The powder and a non-polar dispersant liquid are then wet-milled in

an attritor. The non-polar dispersant liquids disclosed in Serial No. 877,437 are isomerized aliphatic hydrocarbons with an electrical volume resistivity in excess of 10^9 ohm-centimeters, a dielectric constant below 3.0, a vapor pressure at 25°C of less than 10kPa and a Kauri-butanol value in the vicinity of 27 or 28, as determined by ASTM D 1133.

In Serial No. 877,437, the concentrated suspension leaving the attritor is diluted with the same or similar dispersant. During the wet milling or the dilution steps, a novel charge director is added to the suspension. This novel charge director is a neutral species which does not dissociate in the non-polar dispersant liquid until it contacts pigment particles. The diluted suspension is then used to electrophoretically deposit the encapsulated copper particles under space-charge-limited current conditions.

As with all electrophoretic particle depositions, the charged, encapsulated copper particles in Serial No. 877,437 are deposited by applying a voltage. First, a development electrode is placed parallel to the substrate and separated from it by 0.1 to 5 mm, preferably 1 mm. This assembly is then inserted into a bath comprising the particle suspension, and a voltage pulse from a potential source is applied for a prescribed time. The assembly is then removed from the bath, the development electrode separated from the substrate, and the excess liquid removed by dipping the substrate into pure dispersant, by spinning it off, or by passing an air knife over the surface.

Serial No. 877,437 teaches that, once the layer has been deposited, the substrate can be placed onto a heater. The temperature is raised above the melting point of the thermoplastic binder, which causes the binder to flow and fill the interstitial spaces between the discrete, encapsulated particles. Upon cooling to below its melting point, the binder solidifies, resulting in a particle

layer of uniform thickness.

SUMMARY OF THE INVENTION

The present invention relates to the formation of a charge-directed suspension of particles which are electrophoretically deposited onto a substrate under space-charge-limited current conditions. The suspension comprises particles of thermoplastic binder and novel charge director molecules in a non-polar dispersant liquid. These particles may further comprise particles of any one of a myriad of materials that have been encapsulated within the thermoplastic binders. According to the present invention, a variety of layers derived from one of many different types of particles can be deposited under space-charge limited current conditions such that the properties of the particle layer deposited can be controlled.

The particles of the suspension can be deposited so densely under space-charge-limited current conditions that the properties of the resulting particle layer may approximate those properties associated with a continuous layer of the material from which the particles are derived. There are many potential applications for such particle layers. For example, gold, silver, deoxidized copper and perhaps aluminum particles can be encapsulated within the thermoplastic binder to provide highly electrically conductive layers. Thermoplastic binder without an encapsulant provides for a highly insulating particle layer. Particles of aluminum, chromium and other metals, as well as ferroelectric materials, may also be encapsulated to provide for layers useful as dielectric insulators. Partially oxidized copper, and perhaps other metallic particles may be encapsulated within the thermoplastic layer to provide for a thermosensitive particle layer. Particles of lanthanum fluoride and calcium fluoride may be encapsulated to provide for layers having controlled indices of refraction and reflection which are useful in the fabrication of antireflection

coatings and diffraction gratings. Phosphor particles may be encapsulated to provide layers for making cathode ray tubes, florescent coatings for light bulbs, and the like. Particles of lanthanum fluoride may be encapsulated to
5 provide layers which can be used in gas sensors.

A suspension of thermoplastic binder particles in which lead oxide has been encapsulated may be deposited under space-charge-limited current conditions to provide an electron-beam-sensitive layer useful as a sensitive
10 photoresist, while particle layers insensitive to certain etching processes used in the fabrication of integrated circuits may be formed from suspensions comprised of lanthanum fluoride and gold particles. Similarly, encapsulated particles can be electrophoretically
15 deposited from suspensions under space-charge-limited current conditions to form layers of aluminum, boron, arsenic, phosphorus or other materials useful in doping semiconductors. Particle layers useful for curing dislocations in semiconductor substrates, particularly
20 GaAs substrates, can also be formed from particle suspensions of lanthanum fluoride or calcium fluoride.

Layers can also be provided with differing electrical properties, even though the same material is used as the encapsulant. For example, reduced copper particles
25 processed according to one embodiment can be used to provide a highly conductive layer. In fact, a suspension of metallic particles encapsulated in thermoplastic binder deposited under space-charge-limited current conditions may approximate a metal having a very large crystal
30 structure in which numerous conductive pathways are established between adjacent crystals. Conversely, particles having a thick oxide layer can be used to provide for a dielectric layer. Also, as disclosed in Serial No. 877,437, copper particles having a thin oxide
35 layer prior to encapsulation provide for a highly thermosensitive particle layer.

In the present description, the invention is

illustrated by describing the manufacture of a room-temperature solid-state thermal detector imaging array. The basic detector element used in the thermal detector imaging array, illustrated in U.S. Serial No. 877,437, is
5 a bridge structure composed of a layer of partially oxidized copper particles. The present application discloses how to connect an array of these detectors with interconnects formed from an electrophoretically deposited layer of conductive particles. An alternate embodiment of
10 the thermal detector can be built from "islands" of partially oxidized copper particles laid out on a very thin polymeric film. Also described are techniques for constructing p-n junctions, micro-metallic structures, and field-emitting devices, and optical coatings, as well as
15 a technique for the removal of semiconductor dislocations.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows a flow chart for making a particle layer according to the present invention;

Figure 1A shows an apparatus for depositing a
20 particle layer according to the present invention;

Figure 2 shows a thermal detector imaging array formed entirely from particle layers comprised of conductive, insulating or thermosensitive particles;

Figures 3A and 3B illustrate a low pass and high pass
25 filter, respectively, for the thermal detector imaging array shown in Figure 2;

Figures 4, 4A, 4B, and 4C show how bridges can be made from a layer of particles having thermosensitive metal particles as a component to make the imaging array
30 shown in Figure 2;

Figures 5A-5C show how a layer of electrically conductive particles can be deposited and then partially removed atop the thermosensitive toner shown in Figure 4 to form electrical interconnects;

35 Figures 6A-6C show how horizontal electrical interconnects can be deposited on the structures shown in Figures 4 and 5A;

Figures 7A-7C illustrate how to form electrical overpasses using a particle layer formed from electrically conductive pigment particles;

Figure 8 shows a third embodiment of a thermal
5 detector imaging array in which a thermosensitive layer of particles is electrophoretically deposited atop a thin polymeric film;

Figures 9A-9E show a method of doping a silicon substrate using an electrophoretically deposited layer of
10 particles of dopant material according to the present invention;

Figure 10 shows a metallic structure formed from a layer of electrophoretically deposited metal particles; and

15 Figure 11 shows a field emitter made from various particle layers of the present invention that can be used in applications such as a high-definition television (HDTV).

DETAILED DESCRIPTION

20 The process of forming a suspension which can be electrophoretically deposited under space-charge-limited current conditions to form a layer of particles of the present invention is shown in Figure 1. The first step
300 is to micropulverize the material, if any, which is to
25 be encapsulated by the thermoplastic binder. Then, particles of thermoplastic binder, any micropulverized particles (hereinafter called "pigment particles") and other adjuvants are dry milled, step 302, at a temperature above the melting point of the thermoplastic binder.

30 After sufficient milling, the dry mill is shut down. Once the temperature of the mill drops below the melting point of the thermoplastic binder, the encapsulated mixture forms solid, brittle crayon-like substance. This brittle crayon-like substance is then comminuted by any
35 commonly known method, step 304. The comminuted particles of thermoplastic binder (hereinafter called "toner particles", whether or not they encapsulate pigment

particles), are placed into an attritor with a dispersant liquid and wet-milled, step 306. After wet milling, the resulting concentrated suspension can be diluted with additional dispersant, step 308. A novel charge director, 5 which is electrically neutral in dispersant liquid and which does not contain toner particles, may be added during either the dry milling step 302, wet milling step 306, or diluting step 308.

According to our invention, any of a wide variety of 10 pigment particles can be electrophoretically deposited under space-charge-limited current conditions so long as the pigment particles are solid and do not chemically interact with the thermoplastic polymer binder or the dispersant liquid. These pigment particles include 15 carbon, metals, semiconductor dopants and various ceramics. The properties of the electrophoretically deposited particle layer depend on the chemical composition and electrical characteristics of the pigment particles to be deposited. For example, merely 20 incorporating carbon into the thermoplastic binder may produce a photocopier toner suitable for use in conventional copier machines or a particle layer having increased infrared absorption.

For purposes of the present invention, metallic 25 pigment particles can be divided into three categories defined by the electrical behavior. The first type of metallic pigment particles form a metallic layer when deposited under space-charge-limited current conditions and do not have an oxide surface layer when they are 30 encapsulated into the binder. These particles can be used to form electrically conductive layers. The second type of metallic particles have relatively thick oxide layers. The oxide layer on these metallic pigment particles creates a very high direct-current resistance which 35 greatly attenuates electron transfer between adjacent particles. However, the oxidized metal particles remain highly conductive under alternating current conditions.

The third type of metallic pigment particles have thin oxide layers. These oxide layers generally inhibit free electron transfer. Without breaks in the oxide layer, electrons must transfer between particles by thermal activation over the oxide barrier or, for very thin oxides, by tunneling. When the activated mode dominates, i.e., for particles having moderately thin oxide layers, it leads to an exponential change in the electrical conductivity of the layer of particles with a change in temperature. Particle layers comprised of metallic pigment particles with thin oxide layers thus make excellent thermal detectors. For example, in Serial No. 877,437, a thermosensitive material with an exponentially changing resistance resulted from electrophoretic deposition of copper pigment particles having a thin oxide layer under space-charge-limited current conditions.

In the same manner as metal or carbon pigment particles, semiconductor dopants, ceramics, and other pigment particles can comprise toner particles for suspensions deposited electrophoretically under space-charge-limited current conditions to form particle layers. Of course, the properties of the deposited layer will depend on the type of pigment particle deposited. A dense, uniform particle layer is formed as long as the pigment particles which are incorporated into the suspension do not chemically interact with the binder or the dispersant.

The ratio of the pigment particles to binder added to the dry mill is important as it affects the properties desired in the particle layer which is electrophoretically deposited under space-charge-limited current conditions. However, it must be determined experimentally. In general, the pigment particle to binder ratio should be controlled to cover the particles of pigment with a thin layer of binder. Sufficient binder is necessary to cover the pigment particles since only the binder interacts with the charge director to charge the toner particles.

According to the present invention, the thermoplastic polymeric binders used to encapsulate the inert pigment particles may actually be a complex mixture or system of one or more thermoplastic binders. The binder materials must not swell or be soluble in the dispersant liquid at room temperature since swelling increases the viscous drag on the toner particles. This causes the suspension to age and reduces the speed and quality of the electrophoretic deposition of the particle layer. Consequently, preferred binder materials are crystalline polymers or waxes which exhibit a narrow melting range at temperatures above 70°C. It is also imperative that the binders of the present invention contain functional groups which allow the toner particles to interact with the charge director.

A complex thermoplastic binder system according to the present invention comprises A-C 540 (a trademark of Allied Chemical Corporation for ethylene-acrylic acid copolymer), Carnauba wax, and A-C 201 (a trademark of Allied Chemical Corporation for a calcium salt of ethylene-acrylic acid copolymer). Along with functioning as encapsulant for pigment particles, the A-C 540 provides functional sites for the charge director and may help to maintain the appropriate melt viscosity. The second encapsulant material, Carnauba wax, which is a low-melt-viscosity binder having a narrow melting point range, also acts as a lubricant for the pigment particles during the dry milling operation. The third encapsulant, A-C 201, further acts as a dispersing aid during dry milling. However, due to its ionomeric nature (i.e., it is a salt of an acid copolymer), A-C 201 is important to many binder systems since it provides functional sites for the resulting encapsulated pigment particles. In fact, due to its ability to form ionic species in dispersant liquid, A-C 201 is sometimes referred to as a charge director. However, molecules of A-C 201 actually serve as the "hooks", allowing the charge director to attach to the toner particles.

As described above, the most important characteristic of the thermoplastic binder system is its ability to provide a requisite number of functional sites. Consequently, there are several thermoplastic polymers and salts thereof that are added to the binder system, not to encapsulate pigment particles, but to control the number of functional sites on the toner particles. These include stearic acid, styrene-acrylate copolymers, ethylene-vinyl acetate-acrylic acid plus copolymers, oxidized polyethylenes, acrylate ester polymers, acrylate ester-acrylic acid copolymers, styrene-allyl alcohol copolymers, polyethylene oxide polymers, and propylene-ethylene oxide copolymers. Of course, many of these polymers may coincidentally act as encapsulants of the pigment particles.

Other adjuvants (*i.e.*, addition agents), including certain polymeric materials, may be added to the dry mill to effect the properties to the polymeric binders or to enhance the milling operation. For example, polystyrene allyl alcohol (PSAA) and Premix (PSSA reacted with isocyanatoethylanemethacrylate) may be added to the dry mill as dispersing agents. A-C 580, another thermoplastic polymer of the Allied Chemical Corp., can be added to increase the hardness of the binder system. Magnesium oxide can be added to increase resistance to abrasion. Stearic acid is added to further control the number of functional sites. Calcium carbonate and zinc carbonate can be added to the binder system during dry milling to produce ionic crosslinkages among the bonds of the polymer. These ionic crosslinkages, while strong enough to modify the melt viscosity and charge-direction characteristics, are not so strong as to significantly modify the melting temperature range of the binder system.

For many of the proposed uses of particle layers electrophoretically deposited under space-charge-limited current conditions, the binder materials must be cross-linkable upon exposure to light, an ion or electron beam,

elevated temperatures, or other non-chemical means. Consequently, still other adjuvants may be added to the dry mill to impart this property to the toner particles. For example, several of the polymeric binders added to
5 control the number of functional sites coincidentally aid in the ability the binder to form crosslinks. It is important to note that since they are incorporated into the binder system, all adjuvants added to the dry mill must have the same chemical characteristics as the
10 thermoplastic binders, i.e., they must be insoluble and unsolvatable in the dispersant liquid at temperatures below 40°C.

As disclosed in Serial No. 877,437, the dispersant must be a non-polar liquid that does not dissolve or
15 solvate the solids added to the dry mill. Essential characteristics of the dispersant liquid are volume resistivity and dielectric constant. Nonpolar dispersant liquids useful in forming the suspensions of the present invention are isomerized aliphatic hydrocarbons having an
20 electrical volume resistivity in excess of 10^9 ohm-centimeters, a dielectric constant below 3.0, and vapor pressure at 25°C of less than 10kPa. In addition, the dispersants preferably have a low Kauri-butanol value, in the vicinity of 27 or 28, as determined by ASTM D 1133.

25 As similarly disclosed in Serial No. 877,437, preferred dispersants to form the suspensions of the present invention are any one of the several ISOPAR® brand hydrocarbons, in particular, ISOPAR-G, ISOPAR-H, ISOPAR-K, ISOPAR-L and ISOPAR-M. ISOPAR is the trademark for a
30 series of low-boiling narrow cuts of isoparaffinic hydrocarbon fractions, manufactured by the Exxon Corporation. For example, the boiling range of ISOPAR-G is between 156°C and 176°C and it has a flash point, determined by the tag closed cup method, of 40°C. ISOPAR-
35 L has a mid-boiling point of approximately 194°C and a flash point of 61°C, determined by the same method. ISOPAR-M has a flash point, determined by the Pensky-

Martens method, of 77°C and an auto-ignition temperature of 338°C. These hydrocarbons have extremely high levels of purity. Stringent manufacturing specifications limit undesirable components such as sulphur, acids and chlorides in an ISOPAR hydrocarbon to a few parts per million. ISOPAR hydrocarbons are substantially odorless, possess only a very mild paraffinic odor, are not known to be toxic and have excellent odor stability.

Any of several machines can be used to dry mill the toner. A conventional eight-inch, two-roll rubber mill, many examples of which are known in the art, is acceptable. It is believed that the presence and properties of oxide layers surrounding certain metallic pigment particles are a function of the atmosphere above the dry mill. For example, the thermosensitive copper particle layer disclosed in Serial No. 877,437 resulted from dry milling in air. It is further believed that thicker oxide layers should result when the dry mill is operated in oxygen-rich environments, while oxide free metallic particle layers should result from dry milling which takes place under a nitrogen or noble-gas atmosphere. Therefore, the type of machine used should permit one to control the atmosphere during the milling operation.

The order in which the components are added to the dry mill can be quite important. Not only is the size of toner particle affected, but so are the properties of the particle layer which is deposited electrophoretically under space-charge-limited current conditions. However, since the properties of the particle layer are unique to each use, the order and proportions in which the components are added to the dry mill should be determined experimentally. Generally though, when an ionomer is placed on the mill first, followed by the pigmented particles and then other binders and adjuvants, the electrophoretically deposited particle layer will be more uniform.

Once dry milling is complete, the mill is turned off and its contents is allowed to cool. Once below the melt temperature of the thermoplastic binder system, the contents of the mill solidify into a crayon-like mass, which is comminuted by any of several means. The comminuted particles and a non-polar dispersant are then wet milled to form the suspension.

The wet milling can be done with any of several commercially available attritors. It may be preferable to use the minimum amount of dispersant in the wet milling stage to further reduce the overall size of the toner particles. The wet milling of the toner has been known in art for "liquid" toners for some time as exemplified by United States Patent 3,909,433 to Gilliams et al. Since the binder should already encapsulate the pigment particles, the effect of the atmosphere in the attritor should be minimal.

The wet mill should operate for a minimum of several hours, as opposed to the one hour preferred to in Serial No. 877,437. It has been determined that the length of the wet milling can be correlated to the average and root mean square sizes of the toner particles. The longer the wet mill operates, the smaller the average size of the toner particles. For example, when the attritor operates for more than 200 hours, the toner particles for the suspensions of the present invention may have radii of 0.1 microns or less. Also, the size distribution of the toner particles can be made exceptionally uniform if the wet-milling continues for a sufficient period of time, e.g., greater than 100 hours. Importantly, when the toner particles comprise pigment particles, there is still binder coating the discrete particles of pigment. The size of the toner particles becomes a Poisson distribution that is tightly centered around a mean value which can correspond to the size of individual pigment particles. At first, the adhesion of the binder to the pigment particles is generally quite great as the toner particles

inevitably seem to separate along the binder between the toner particles rather than by splitting the particles of pigment. Extensive milling, however, can strip the binder from the particles which then must be recreated, typically
5 in the wet mill.

Encapsulated metallic pigment particles of our invention can be as small as 100 Angstroms in diameter, which is between the size of crystalline metal and amorphous metal. Consequently, the conductive pathway
10 through the metallic particles is more circuitous than it would be through a comparable layer of homogeneous material. However, there are many more electrical connections between the discrete particles of our particle layers than between comparable particles in a
15 conventional, paint-type coating, or particle layers which are deposited according to the electrophoretic methods of the prior art. More importantly, the resistance of particle layers of the present invention is more predictable and reproducible than for prior art particle
20 layers. These characteristics enable the deposition of conductive metallic particle layers useful as electrical interconnects not available using prior art encapsulated particles layers.

According to the present invention the charged
25 encapsulated pigment particles should be electrophoretically deposited under space-charge-limited current conditions and under conditions that avoid continuous phase conductivity of the charge-directed suspension. The suspension can be conceptualized as a
30 plasma of charged, encapsulated pigment particles and counter ions in which the mobility of the particles is determined by drag with the adjacent dispersant liquid. In the suspension, the oppositely charged counter ions move faster because they are much smaller and experience
35 less drag than the larger toner particles, even if the toner particles acquire several charges. Under space-charge-limited current conditions, applying an electric

field creates a depletion region above one electrode as the more mobile counter ions quickly move toward the opposite electrode. It is possible to over charge direct the toner particles by placing so many charges on the particles that their mobility exceeds the mobility of the counter ions. In this case, the toner deposits first leaving a depletion layer consisting of counter ions. As a result, the toner particles do not deposit under high-field space-charge-limited conditions, and packing densities and uniformity are reduced. This condition must be avoided. The suspension attains a net total charge in the depletion region, whereas the pigment particles and counter ions cancel each other in the rest of the suspension. Hence, the pigment particles in the depletion region experience a strong electrostatic attraction towards the electrode. However, the coulombic repulsion among the pigment particles produces an electrostatic gradient in the depletion region. The first pigment particles to reach the electrode repel later arrivals. Areas of the electrode not covered by pigment particles, however, do not repel additional pigment particles. In this way, the encapsulated pigment particles distribute themselves evenly over the surface of the electrode as long as the electrostatic field is applied. The deposition of the encapsulated pigment particles out of the transient depletion region of the suspension is believed to be an important factor contributing to the high particle density achieved by our invention.

The coulombic repulsion among the toner particles also prevents agglomeration of the encapsulated particles in the suspension. The toner particles remain uniformly distributed in suspension since uniformity has the lowest energy state with respect to the coulombic repulsion between the individual toner particles. This coulombic repulsion keeps the toner particles separate so long as the temperature of the toner is not too high for too long. The uniform distribution of the toner particles in

suspension transfers to the substrate. Hence, toner particles are electrophoretically deposited more uniformly on the substrate under space-charge-limited current conditions than would occur if the toner particles were
5 deposited electrophoretically under continuous phase conductivity conditions or non-electrophoretic means such as aerosol spraying or painting.

Novel charge directors of the type disclosed in Serial No. 877,437 are essential in allowing the
10 electrophoretic deposition of particle layers under space charge limited current conditions. The novel charge directors of the present invention, e.g., barium sulfosuccinate (BaOT) and barium salts of bistridecyl sulfosuccinate (Batri) have essentially no conductivity in
15 pure ISOPAR. This conductivity increases drastically when toner particles are added. On the other hand, charge directors of the prior art, e.g., lecithin and barium petronate (BaPet), when mixed in pure ISOPAR have a conductivity measured at 1 khz, which is greater than the
20 conductivity of these suspensions when toner particles are added.

When the novel charge directors of the present invention are used, the number of charge director ions is then proportional to the number of functional sites on the
25 encapsulated pigment particles. Thermal equilibrium between the charge director molecules and the binder on the toner particles ensures that the problems of continuous phase conductivity and toner exhaustion are avoided and optimal electrophoretic deposition occurs.

30 The novel charge directors of the present invention can be added with the toner particles and the dispersant to the wet mill, or they can be added to the suspension during the dilution step. Moreover, the novel charge director may also be added to the dry mill, which provides
35 for internal charge direction.

The addition of small amounts of charge director on the dry mill greatly increases the efficiency of charge

direction. In particular, Batri, and/or barium ditridecyl sulfosuccinate, provide advantages when added onto the dry mill. While the exact mechanism is not known, we believe that charge director introduction during dry milling
5 causes the formation, in situ, of additional ionomeric species, which provide for additional functional sites. Our hypothesis concerning the in situ formation of ionomeric species is supported when other salts of bistridecyl sulfosuccinate, e.g., sodium bistridecyl
10 sulfosuccinate (Natri), are incorporated onto the mill. In such instances, the ratio of the polymeric binders and adjuvants must be adjusted to compensate for the change in melt viscosity, probably caused by the in situ ionomer formation on the mill. Moreover, we have experimentally
15 determined that ionomers produced from alkali or alkaline earth metal salts may well exhibit melt viscosities inversely related, in part, to their ionic radii.

Unexpectedly, we have discovered that the addition of charge director during dry milling of carbon-based toners
20 provides for smaller encapsulated pigment particles. We believe that this smaller ultimate particle size is due to the increased dispersion achieved on the two roll mill, since attrition merely induces cohesive failure in the polymer-wax binder itself. In fact, we believe that one
25 way to take advantage of the smaller ultimate size of the encapsulated pigment particle is to incorporate Batri, or a like charge director into the two roll mill at levels insufficient to impart substantial charge direction, but at levels sufficient to reduce the effluent particle size
30 after attrition.

After wet milling, the depositing step is carried out in a bath containing the encapsulated particles which have been charge-directed. The drift velocity of the particles is a function of the applied field. The higher the field,
35 the more rapid is the drift velocity. Since the thickness of the depletion layer is a function of potential, and since only the particles in the space charge region are

deposited quickly, varying the potential or the deposition time enables us to control the thickness of the deposited layer. If we are depositing on a metal disk, for example, we may use a potential of between 400 volts and 1000 volts with the metal being connected to the positive electrode. The time of subjection to the field may vary between .0001 and 1 second. Alternatively, insulators can be made by first subjecting the substrate to a corona charging step and then passing the charged medium through a development region to attract toner.

Substrate deposition has been accomplished in a number of different ways. Referring to Figure 1A, a development electrode 2 is placed parallel to the substrate 4 and separated from it by 0.1 to 5 mm. The separation is usually placed at 1mm. The assembly is then inserted into the toner bath 6 in a container 3, and a voltage pulse from a source of potential 8 is applied for an experimentally-determined time via switch 5. The assembly is then removed from the bath, the development electrode is separated from the substrate, and the excess liquid is removed by dipping the substrate into pure ISOPAR, by spinning it off, or by passing an air knife (not shown) over the surface.

With the toner of the present invention, particle deposition can be conducted using xerographic techniques well known in the art. for example, a charged photoconductive element, such as a drum, can be exposed with an image of a desired pattern, selectively discharging those regions which have been illuminated. The photoconductive element is then exposed to the toner suspension of the present invention, with the charged regions of the element attracting oppositely charged toner particles. The resulting pattern can then be transferred to a substrate. This technique should be effective in the manufacture of circuit boards, particularly flexible circuit boards.

The layer of particles electrophoretically deposited

under space-charge-limited current conditions is far more dense than those obtained by other methods, e.g., electrophoretic deposition occurring under continuous phase conductivity which yields a loosely-packed random
5 distribution of particles. The particle layers of the present invention can be made still more dense by heating it until the thermoplastic polymer binder melts, which causes the thermoplastic binder of adjacent toner particles to fuse. The fusing further reduces the
10 interstitial space between the individual toner particles. Moreover, melting causes some of the binder covering the pigment particles to flow into the interstices between particles, allowing for some direct contact between pigment particles. The particle layer must not be heated
15 so far above the melting temperature of the binder so as to crosslink it, since crosslinking prevents the easy removal of portions of the particle layer during its subsequent fabrication. The binders of choice for the present invention typically soften at temperatures above
20 70°C, but do not crosslink until reaching temperatures of between 100°C and 130°C.

The electrophoretic deposition of particle layers under space-charged-limited current conditions is particularly useful in forming layers of conductive metal
25 particles such as silver and gold. The increased packing density of the particles, together with the increased pigment particle contact, decreases the electrical resistance of the particle layer. The resistance of the particle layer decreases with increasing toner particle
30 wet-milling time up to the point where the sizes of the metal particles no longer decrease. This is consistent with an increase in the number of electrical contacts between the particles, resulting from a decrease in the average size and size distribution width of the toner
35 particles.

For several uses contemplated for the electrophoretically deposited particle layer of the

present invention, adjacent molecules of the thermoplastic binder must be crosslinked. A fused layer of particles can be written upon using an electron beam, light, heat, or any other technique that can crosslink adjacent polymer molecules. Exposure to an electron beam is usually preferred, however, since the very small cross-section of the beam width allows the writing of very thin patterns on the particle layer and particles are at least partially transparent to the beams permitting the binder under the top layer of particles to be exposed. When used to write upon the particle layer of our invention, the energy of the electron beam must be sufficient to crosslink the adjacent binder molecules, but not so great as to destroy them. Alternately, as with exposing photoresistive materials, the particle layer may be exposed to light in the infrared, visible or ultraviolet spectrum to establish a pattern. Once the desired adjacent binder molecules have been crosslinked, the particle layer may be developed so that the non-crosslinked portions of the particle layer are removed from the substrate. Methods of removal for this purpose are well known in the art.

If the exposure and development of the particle layer is used in the fabrication of IC chips, the preferred method of exposure is an electron beam which produces very small structures. Using the present invention, features one micron wide can be reproduced by using an electron beam having a diameter of one micron and an energy of 10 keV operated at a current of 2 nanoamperes. In fact, after a layer of metallic pigment particles, e.g., copper, has been heated to a temperature above the softening point of the binder molecules, a one micron line, with an edge resolution of 0.1 micron, can be written with an electron beam. Such resolution should not be interpreted as a maximum, since better resolution should be possible; the minimum width of a line exposed by an electron beam should approach the resolution limit set by the diameter of the particles comprising the particle layer.

It is possible to form bridge structures using a relatively thick particle layer deposited according to our invention. A more-energetic electron beam can be used to write the bridge support structures, while a less-energetic electron beam written between adjacent supports forms the span. The less energetic electron beams are used to crosslink adjacent binder molecules near the surface of the particle layer without crosslinking these binder molecules near the particle layer/substrate interface. In such instances, the particle layer beneath the span of the bridge can be developed and removed. It is important not to heat the particle layer much above its softening point, because even minimal crosslinking in unexposed areas will create enough of an attraction between the bridge span and the unexposed portions of the particle layer below it to prevent development of the latter.

A further consideration in the exposure and development of particle layers of the present invention is the adhesive forces between the binder molecules and the substrate upon which the particle layer has been electrophoretically deposited. For example, silicon oxide (SiO_2) exerts an adhesive force on the binder materials that can, in some instances, prevent removal of unexposed binder molecules from beneath the spans of certain bridge structures. This problem can be overcome by spin-coating a conventional negative photoresist onto the silicon substrate before electrophoretically depositing the toner. An acceptable resist is sold under the trademark R747v, which is manufactured by Kodak. The thickness of the negative photoresist should be kept minimal, however, because it has a different thermal expansion coefficient than the particle layer which can cause "mud cracking" of the particle layer when it is cured rapidly by heating. A suitable negative-resist stripper will remove the particle layer from the unexposed areas when developed at 75°C for a relatively short period of time.

Figure 2 shows a thermal detector array constructed according to the present invention. This array can be made entirely from three layers of particles -- one layer comprised of thermosensitive metallic particles and two
5 layers comprised of electrically conductive metallic particles that form overlapping electrical interconnects. In this example, all interconnect crossovers are made within the detector array. Of course, it is also possible to design the interconnects in an interdigitated
10 arrangement such that the appropriate electrical crossovers occur outside the array.

The imaging array shown in Figure 2 has sixteen bridges with spanning sections 1-16, each corresponding to a pixel, arranged in a four by four matrix. The bridges
15 are formed by electrophoretically depositing, according to our invention, a layer of thermosensitive pigment particles. A plurality of horizontal interconnects 21-24 along with vertical sections 21'-24' and horizontal sections 21"-24" form an electrical connection to one side
20 of each bridge span. Vertical interconnects 51-54 and stubs 51'-54' form electrical connections to the other side of the spans. FET transistors 41-48 control the conductive state of each of the respective horizontal and vertical interconnects. Transistors 41-44 electrically
25 connect horizontal interconnects 21-24 to a voltage Vcc. The gates of transistors 41-44 are connected to a driver circuit 49. Transistors 45-48 can similarly connect vertical interconnects 51-54 to generate an output signal. The gates of transistors 45-48 are connected to a driver
30 circuit 50. Driver circuits 49, 50 can comprise conventional shift registers, the construction of which is known in the art.

The thermal detector imaging array shown in Figure 2 can measure the electrical resistance of each pixel
35 separately along a serially multiplexed output line 55. For example, transistor 41 can be turned on so as to provide a voltage to bridges 1-4. Transistors 45-48 can

be turned on one at a time. The output signal is thus indicative of the electrical resistance of the respective bridge. The electrical resistance indicates the temperature of the corresponding pixel and is a function of the amount of infrared radiant energy the bridge absorbs. The resistance of the bridges can be measured, one pixel at a time, across the entire imaging array. The output signal can be measured as a voltage signal using the low pass filter shown in Figure 3A. Alternately, a high pass filter of the type shown in Figure 3B can be used if a chopper is used with the array rather than, or in addition to, the voltage signal. The current in the output signal could also be evaluated.

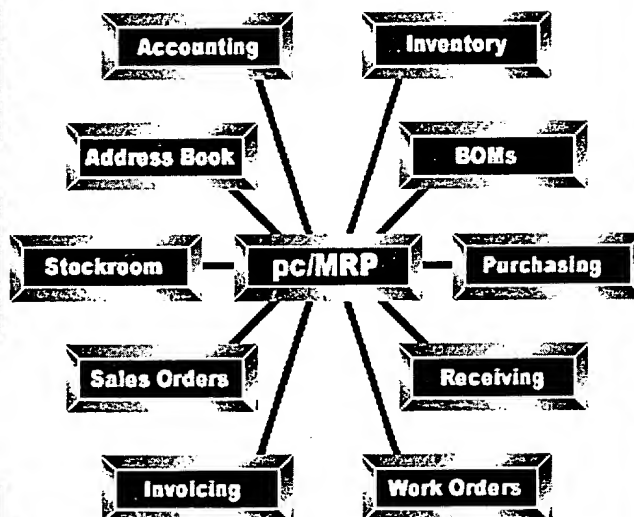
It is to be appreciated that the thermal detector imaging array shown in Figure 2 is only exemplary. The size of the imaging array could be expanded as desired and the size of each pixel can be expanded so long as the bridge spans do not break. Large imaging arrays with small pixels produce better resolution and are therefore preferred. The rate at which the array can operate is a function of how fast the individual bridges can change their electrical conductivity and how fast their voltage values can be read out. U.S. Serial No. 877,437 demonstrated a bridge span with four support legs. Such a table top bridge can rapidly change its temperature in response to changes in incident illumination. The bridge structures used to form the pixels in Figure 2 differs in that the supports cover an entire side of the bridge span. These bridges should also have a reasonably low thermal capacity so that they can change temperature reasonably quickly. The bridges shown in Figure 2 are also easier to make. A capacitive loading on the output lines as well as on the bridges themselves may limit the maximum frequency of the output signal for large arrays. These considerations, however, are commonly encountered in designing any imaging array. The array shown in Figure 2 represents a particularly simple infrared sensor that is

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made entirely of electrophoretically deposited particle layers and that functions at room temperature.

Figures 4-6 illustrate the steps needed to make the thermal detector imaging array shown in Figure 2 by electrophoretically depositing three particle layers. The order in which these steps are performed is not the object of this invention; rather, the present invention is directed toward the electrophoretic deposition and use of particle layers needed to make an imaging array work and how the particle layers function in an operable thermal detector imaging array.

Figure 4A illustrates a layer 101 of thermosensitive metallic pigment particles deposited on a substrate 103 by electrophoretic deposition according to the present invention. The thermosensitive particles have a partial oxide layer and produce the behavior that is described in our previous application -- an exponential change in electrical resistance with a linear change in temperature. The partial oxide layer covering the metallic pigment particles can be formed by operating the dry mill in an atmosphere of ordinary air. The hot rolling in the two-roll mill appears to generate a thin oxide layer on the metallic particles that is responsible for the observed exponential change in resistance with a linear change in temperature. The metallic particles encapsulated by the thermoplastic binder described above are preferably on the order of 1-20 microns in diameter.

Figure 4B shows the step of writing on particle layer 101 with an electron beam 104 to make the bridges for the thermal detecting imaging array of the present invention comprised of a layer of thermosensitive pigment particles. The rows of bridge supports 35-39 represent portions of exposed areas 101a where the particle layer has been exposed all the way to its interface with the substrate 103. These rows can be formed with a continuous motion of the electron beam 104 or through exposure to light using an appropriate photolithographic mask, examples of both

are known in the art. The bridge spans 1-4 represent portions of exposed areas 101a that partially extend to the interface, forming the horizontal rows 20b shown in Figure 4. The areas 101b remain unexposed. The exposed areas 101a become crosslinked as noted above.

The exposed particle layer 101a is then developed using a conventional developing agent, such as toluene, in a conventional development process to remove the unexposed portions 101b of the particle layer. The supports 35-39 remain attached to the substrate. The bridge strips 20b in Figure 4 remain attached to supports 35-39 and form the bridge spans 1-16. Trenches 20a in Figure 4C are formed below the bridge spans 1-4 and between the bridge supports 35-39. The width of the spans must be small enough and the separation of the spans must be great enough to facilitate removal of the unexposed encapsulated particles from underneath the bridge spans. It is also desirable to maximize the surface area of the bridge spans. As the span width and surface area of the bridge spans are trade-offs, both considerations should be balanced in forming the bridges. Further, the thickness of the bridge spans can be substantially less than the height or width of the supports. In fact, thin bridges are actually preferred because they both reduce the heat capacity and thermal conductivity of the pixel and thus they require less exposure of the particle layer.

The bridge spans 1-16 have less heat capacity than would the same material if applied directly to substrate 25. The response of the bridge spans when used as pixels in an imaging array is governed by the heat capacity of each span. Minimizing the heat capacity of the bridge spans thus maximizes the response rate of the imaging array. This objective is best obtained by providing for an intervening layer of insulating air between the thermosensitive bridge spans and the substrate. By such an arrangement, the heat capacity of the substrate does not contribute to the heat capacity of the bridge spans.

Moreover, the heat capacity of the supports will not contribute significantly to the total heat capacity of the bridge spans.

Bridge structures have been fabricated using an electron beam to expose the appropriate regions of a particle layer deposited according to the present invention. The bridge spans correspond to those parts of the imaging matrix that were exposed with a less energetic electron beam than the electron beam used to form the bridge supports. By varying the energy of the electron beam while writing, alignment problems associated with corresponding multi-step lithographic techniques can be avoided. In Figure 4A, the bridge supports 35-39 correspond to vertical movements of a higher energy electron beam, whereas the bridge spans 1-16 are made using horizontal movements of a less energetic electron beam.

Since the environment around the thermal detector also emits infrared radiant energy, another consideration in building the imaging array is the effect of thermal exchange noise (TEN) on performance. The thermal detector made with layers comprised of thermosensitive pigment particles are broad-band detectors that are sensitive to virtually the entire infrared band. The imaging array shown in Figure 4 is not cooled and is intended to operate at room temperature. Since the infrared emissions from the environment in the immediate vicinity of the thermal detector imaging array produces the type of long wavelength infrared radiation that the detector is designed to measure, TEN creates random fluctuations in the measured voltage that can degrade the image.

One solution to minimizing TEN is to average the signals from several pixels. The random changes in the signal caused by thermal exchange noise will not effect all pixels the same way at the same time. As demonstrated in Serial No. 877,437, TEN decreases with the square root of the number of bridges that comprise each pixel. There

are at least two ways to accomplish this type of noise reduction. One way is to replace each of the bridges 1-16 as shown in Figure 2 with a plurality of bridges by drawing an electron beam of lesser width horizontally several times. These bridge spans can then be connected in parallel so that the measured emf derives from several bridges at once.

A second way is to electronically average the signals from a plurality of the bridge spans. For example, the array shown in Figure 2 could comprise a single pixel. The resistance values for each of the bridge spans could be measured and statistically averaged to produce a net value for the given pixel. The noise in the signal could be reduced by at least a factor of four without employing any statistical corrections to eliminate widely deviant pixels from the computation. Such calculations which would be needed to perform these measurements are known in the art.

Experiment has shown that the bridge spans exhibit good mechanical stability. One micron thick bridge structures have shown the ability to span up to a width of 40 microns. Any mechanical instability in the bridges should be overcome by establishing a central support for the bridge by, for example, exposing the center of the span to a small, high energy beam of electrons to crosslink the binder through to the substrate base and create a pillar in the center of the bridge which would prevent sagging. As previously discussed, the mechanical stability of our bridge structures are a function of the particles used to create the thermosensitive particles layers used in the thermal detector.

The ability of the bridge structures to absorb infrared radiation can be enhanced by incorporating particles of dye into the encapsulated pigment particles. For example, carbon particles are useful for this purpose since they absorb infrared radiant energy and are sufficiently poor electrical conductors so that the

resistance of the bridge structures is decreased only slightly.

To obtain the structure of Figures 5A-C, a first layer of conductive material is used to form electrical interconnects for the thermal-detecting imaging array shown in Figure 4. Then, a particle layer of our invention wherein the pigment is comprised of conductive pigments, e.g., silver or gold, which do not readily oxidize in air, is deposited over the structure of Figure 4. Alternately, the conductive pigments may be copper particles so long as any layer of surface oxide has been removed before encapsulation, e.g., by a stream of hydrogen gas heated to below the temperature that is needed to sinter the copper. Subsequent dry milling should then be conducted under an oxygen-free atmosphere. Once the conductive particle layer has been exposed, the array is developed so that the toner in the unexposed areas is removed to obtain the results shown by Figures 5A-C.

As illustrated in Figure 5A, a strip of the deposited conductive particle layer is exposed on each side of the top of a support between alternating rows of pixels to form interconnects 51-54. The conductive interconnects 51-54 are also shown in Figure 2. Conductive islands 65-76 shown in Figure 5A are exposed between the bridge spans on alternating supports opposite conductive strips 51-54. These electrical islands help establish electrical contact with the horizontal interconnects 21-24 of Figure 2, as will be described below.

Figure 6A shows the second layer of overlapping electrical interconnects for the thermal detecting imaging array shown in Figure 2. A second particle layer of our invention, having conductive particles as pigment, is deposited over the array shown in Figure 5A. Horizontal interconnects 21-24 of Figure 6A are exposed along respective rows of bridge spans 1-16 and extend through trenches 20a as shown in Figure 6B. The interconnects 21-

24 also overlay conductive islands 65-76 shown in Figure 5A. Conductive islands 102-113 are exposed on top of conductive islands 65-76 to form electrical interconnects between strips 21-24 and the bridge spans 1-16, i.e., the horizontal interconnects 21-24 also form electrical connections with conductive islands 65-76. Conductive islands 86-101 between interconnects 21-24 are also exposed to establish connections between conductive strips 51-54 and bridge spans 1-16 (Figure 6C). Islands 86-89 connect interconnect 51 to bridges 1, 5, 9, 10 and 13 as shown in Figure 6A. Likewise, islands 90-93 connect interconnect 52 to bridges 2, 6, 10 and 14; islands 94-97 connect interconnect 53 to bridges 3, 7, 11, and 15; and islands 98-101 connect interconnect 54 to bridges 4, 8, 12, 16.

The particle layer may be exposed to form the electrical contacts using an electron beam as it is moved horizontally. Alternately, the particle layer may be exposed photolithographically using a mask that can be exposed by light. Where interconnects are to be made between the first and second conductive particle layers, the second conductive particle layer is exposed (crosslinked) all the way to the underlying first conductive particle layer.

The structure shown in Figures 6A and 6B also requires that the second conductive particle layer form horizontal conductive strips 21-24 that overlap the vertical conductive strips 51-54 without establishing electrical contact. Several methods for avoiding electrical contact are discussed in Figures 7A-7C and will be explained below. One way of obtaining the overlapping electrical interconnects is shown in Figure 7A. A relatively thick particle layer 120, having conductive metal particles as pigment, is electrophoretically deposited over the substrate 103, supports 35 and 36, and conductors 51, 52 and 66. The particle layer is exposed all the way to the substrate in the trough between

supports 35-36 and all the way to support 35 and conductor 66 thereon. Adjacent to and over support 36 and conductors 51 and 52 thereon, the exposure energy is reduced so that only the portion of the particle layer close to its surface is exposed. The result is a bridge span 121 over and spaced from the vertical conductive strips 51 and 52. If scanning from left to right with an electron beam, full exposure can be maintained to a point just before support 36, for example. Then only the surface layer is exposed over support 36. Maximum exposure of the particle layer may then resume until the next bridge structure. Alternately, the maximum exposures and the less energetic bridging exposures can be made in separate steps. After exposure, the layer is developed resulting in the pattern of Figure 7A. However made, bridge span 121 is an overlapping electrical interconnect that keeps the electrical interconnects made from the second particle layer from contacting the underlying conductive strips 51 and 52 that were fabricated from the first conductive particle layer.

The electrical connection shown in Figure 7A has the possible disadvantage that the bridge span 121 might form a region of high resistance along the horizontal connector due to the reduced cross section of the interconnect. It may be undesirable to have such a resistance in close proximity to the thermal detecting elements. Thus, Figure 7B shows an alternative construction of the overlapping electrical interconnects in which the electrical connection is a bridge supported by pillars 122 that are periodically "punched" down to the substrate by periodically increasing the energy of the electron beam. Since the entire length of the interconnect is essentially the same thickness, this "aqueduct"-type interconnect eliminates the possibility that the bridge spans 121 could function as local resistors that would establish discrete capacitances along the interconnect. If desired, connections to the substrate could also be made using the

support columns.

The embodiment of Figure 6B also avoids local resistors since this embodiment uses a thinner conductive particle layer 120. As shown in Figure 7C, this embodiment may be made to have an intervening insulating particle layer 130 to separate the bridge span 121 from the vertical conductive strips 51 and 52. The insulating particle layer is a separate particle layer deposited, patterned (exposed) and developed between the first and second conductive particle layers. The thickness of this insulator layer would be controlled in the same way as any electrophoretically deposited layer of particles according to our invention, i.e., by regulating the concentration of encapsulated pigment particles in the suspension and the duration and magnitude of the electrostatic field used to deposit the particle layer.

A direct-current insulating layer 130 can be formed using pigment particles having a thick oxide layer milled with the thermoplastic polymer binder or using the binder alone. For example, aluminum and chromium form a thick oxide layer when milled with the binder in an atmosphere of air. The insulator can thus be used to separate electrically conductive coatings from conductive layers as well as from the thermal sensitive layers on the supports. No d.c. conductivity has ever been measured for such a layer of metallic particles.

Figure 8 shows a third embodiment of a thermal detector imaging array in which a thermosensitive particle layer is exposed to form areas of thermosensitive pigment particles 114 and 115 on a polymeric film 116. The thermosensitive areas are connected by conductive electrical interconnects 117-119 in the manner of Figure 2. Conductive interconnects may be comprised of conductive particle layers or other types of electrical interconnections known in the art. The polymeric film 116 is preferably very thin so as to have a low heat capacity such that pixels 114-115 can rapidly change their

temperature and, hence, also their electrical resistivity. A suitable film is Hostphan RE polyester manufactured by Hoechst Celanese Polyester Film Division in Greer, South Carolina. This polyester film has a thickness of 1.5 to 5 3.5 microns and a correspondingly low thermal capacity. Other thin films should be suitable for use in this thermal detector, including conventional thin polymer films such as Mylar®.

The primary advantage of the thermal detector imaging 10 array shown in Figure 8 is its simplicity of manufacture. The thermosensitive particle layer used to form the thermosensitive areas 114 and 115 can be deposited and interconnected without having to be fabricated into a bridge structure. Connection can be established between 15 interconnects 117-119 and the thermosensitive regions using the techniques discussed in Figures 7A-7C. Interconnect 118 can also be isolated from interconnects 117 and 119 using the techniques discussed in connection with these Figures.

20 Particle layers deposited under space-charge-limited-current conditions should also be particularly useful in the manufacture of an integrated circuit. While there are many ways to manufacture an IC, all involve laying down a layer of photoresist to protect certain underlying regions 25 from processing steps such as ion implantation, etching, metallization, etc. A different layer of photoresist is laid down for each different level of the IC chip. The dimensions of the structures to be fabricated are only a few microns wide. Having to repeatedly align these masks 30 across an entire wafer poses a major alignment problem as chip size continues to decline.

Another problem in reducing the size of IC chips is that of establishing overlapping, electrically isolated, electrical interconnects. Any complex, two dimensional 35 electrical circuit will need to have electrical interconnects that cross one another without making electrical contact. These interconnects also need to have

a low electrical resistance since the electrical resistance will determine the RC time constant of the interconnect and, thus, the speed at which a signal can propagate down the interconnect. Interconnects having low
5 electrical resistance are those formed from layers of metal such as pure aluminum or aluminum alloyed with small amounts of copper. Metal interconnects, however, are difficult or impossible to overlap without establishing electrical contact. Hence, IC fabrication typically uses
10 metallic interconnects in only one direction; the crossing interconnects are silicon based, e.g., polysilicon or silicon regions that are doped with materials such as phosphorus. These nonmetallic interconnects, however, have a higher resistance than metallic interconnects and,
15 therefore, are restricted in length to avoid undue delays during operation of the IC.

One proposed use of the present invention is the formation of electrical interconnects for integrated circuits using the techniques associated with the
20 construction of the thermal distributor in FIG. 2. A layer of particles electrophoretically deposited according to the present invention can be exposed and developed to form the electrical interconnects for integrated circuits. First, in an exposure step, a pattern can be written upon
25 a layer of particles of the present invention to crosslink adjacent polymer molecules. The particle layer is then developed.

By repeatedly exposing and developing particle layers that have been electrophoretically deposited according to
30 the present invention, bridge structures important to the proper function of integrated circuits can be formed. Such structures can span between supports that are formed by differentially exposing different areas of the particle layer. The supports for such a bridge are formed by
35 exposing the particle layer completely through to the underlying substrate. The spans of the bridges can be formed by exposing only the top region of the particle

layer.

The unexposed particle layer from under the bridge span can be removed by merely developing the particle layer; the supports remain attached to the underlying substrate and the bridge spans remain attached to the supports. In this way, it should be possible to form whole networks of overlapping electrical interconnects above an underlying integrated circuit in which the electrical interconnects are separated from one another by layers of insulating air. Certain IC applications require long lines of overlapping interconnects. It should be possible to make long electrical interconnects according to our invention where the conductive particles are so densely packed that the overall electrical resistance of the interconnect is quite low.

One application relates to the RAM memory units that contain large matrices of overlapping interconnects. Read and write lines extend to each memory cell, typically a capacitor and controlling transistor, on an x-y grid of orthogonal, overlapping interconnects. The length of each interconnect is ideally the same as the dimensions of the entire memory unit. The relatively high resistance of the silicon based interconnects, however, will slow the memory unit unless the interconnect length is kept small. The only good way to keep down the length of the silicon-based interconnects is to connect shorter lengths to orthogonal, conductive interconnects. When silver or deoxidized copper particles are used as the interconnect material, the resistance of the interconnect should be reduced relative to conventional aluminum interconnects. In addition, if the particle layer is heated so as to drive off the binder, and then heated further to sinter the metallic particles, one should obtain interconnects which approximate those made from solid micrometallic structures.

Another application needing highly conductive, overlapping interconnects is in the fabrication of high

resolution solid-state imaging devices, such as the thermal detector shown in FIG. 2. In such devices it critical to have a regular, uniform positioning of each imaging pixel.

5 Yet another application needing highly conductive, overlapping interconnects is in the fabrication of microprocessors. Microprocessors need thousands of electrical interconnects. The dimensions of these interconnects are already at or below one micron in size.
10 There would be tremendous benefit in simplifying the design of microprocessors by permitting long, overlapping interconnects. More transistors could be placed in the same area since external conductive electrical interconnects could be dispensed with. Moreover, easier
15 interconnect fabrication would help reduce the problems of misalignment that can greatly reduce the yields in manufacturing microprocessors; yields in IC fabrication of ten percent or less are common due, in large measure, to misalignment of the photoresist masks. Processing speeds
20 of microprocessors can also be increased by using more-conductive electrical interconnects.

Figures 9A-9E illustrate doping a silicon substrate using electrophoretically deposited particle layers of the present invention. The particle layers have pigments
25 comprising particles of materials usually used to dope a semiconductor substrate. Figure 9A illustrates using these particles layers to make a simple p-n junction. It should be apparent that semiconductors other than silicon can be doped using this technique.

30 In forming a p-n junction, the silicon substrate must be doped twice. The present invention proposes to separately dope the n- and p-regions of the substrate by electrophoretically depositing layers comprising each type of the dopant particles. First, a layer of pigment
35 containing an n-type dopant (e.g., P, As, Sb, Bi) is deposited, exposed, and developed to obtain a structure 140 on substrate 141 (e.g., silicon), as shown in Figure

9A. Doping proceeds by first depositing a particle layer having the dopant as pigment. The particle layer is then exposed using light, an electron beam or any other means to crosslink adjacent molecules of binder in the desired doping region. After developing, the structure 140 is heated to drive off the hydrocarbon polymer. Heating continues until the n-type dopant particles diffuse into the silicon substrate to form the structure shown in Figure 9B having a doped area 144. The unused dopant 142, if any, is then stripped to leave an n-type region 144 as shown in Figure 9C. Now p-type material (e.g., B, Al, Ga, In) is deposited, exposed, developed and heated to form the sintered layer 146 of Figure 9D. This is further heated to diffuse the p-type dopant and stripped of any unused dopant to obtain the p-n junction of Figure 9E, with an n-doped area 144 and a p-doped area 148. The silicon is then oxidized in accordance with known techniques to form a layer of silicon oxide, passivating the substrate.

20 To form the electrical connection, the layer of silicon oxide must then be etched to expose the underlying substrate. This etching can be done in a conventional manner by applying a photoresist, exposing, developing and then etching the oxide. Alternately, the etching may be done according to the present invention by depositing a layer of binder particles and crosslinking these particles in all areas but the area to be etched. The layer is then developed and etched. The crosslinked layer prevents etching of the oxide. Next, the electrical interconnects for the p-n junction can be established by depositing a layer comprised of conductive pigment particles as described above. The layer of conductive particles (e.g., silver) is exposed in the area desired to form the electrical interconnects and then developed such that the layer of conductive particles extends to the silicon substrate in the regions to be connected.

This process is advantageous in that the chemicals

used in the present invention are primarily thermoplastic polymers and hydrocarbons that are not known to be toxic. The polymer binders are waxes and rubbers and the dispersants used to suspend the encapsulated pigment particles are common cleaning fluids. Moreover, the dopant layers are visible prior to sintering, making it possible to inspect the accuracy of the photolithographic alignment prior to doping and to identify defects in the IC chip prior to final fabrication. Further, the physical presence of the doped layers atop the silicon substrate facilitates proper alignment since the patterns of the layers to be deposited can be aligned with layers already deposited. Such reference markers should increase production yields significantly.

The formation of micrometallic structures is another possible use for metallic particles layers. Figure 10 shows one such structure in which a beam 201 extends from a support 200. This structure can be formed by depositing, exposing and developing a layer comprised of metallic particles as described above. The exposure energy should be controlled such that the particle layer is crosslinked to the substrate surface in the support 200 region, while only the surface of the particle layer is crosslinked for the beam 201 region. The particle layer is then developed and sintered, i.e., it is heated to 300°C to evaporate the binder. The remaining metal particles are fused by rapid heating to form a microstructure made entirely of metal. This type of metallic structure is analogous to the microstructures made from silicon used to form micromachines as well as electrical interconnects.

The suspended beam shown in Figure 10 has utility as an optical modulator. The beam can be biased to a different voltage than the substrate, creating an electrostatic attraction that bends the beam. A light ray impinging on the upper surface 202 of the beam 201 will therefore be deflected at a controllable angle. Such

structures can be manufactured into an array in much the same manner as described above in connection with Figures 2-7.

Figure 11 illustrates an application of the present invention to the fabrication of a field emitter having optical display applications. In this embodiment, a silicon substrate 400 supports a metal particle layer 402 having a multiplicity of points. A metal conductor 404 forming two bridges 408 over the particle layer 402 is separated from the layer 402 by insulating supports 406. Applying a sufficient positive voltage between the substrate 400 and the bridges 408 causes electrons to be field emitted from the metallic points on the substrate.

If a larger potential is applied between the substrate 400 and a region above the surface (for example, a phosphor layer), an electrical field is established. This causes the electrons to be accelerated to the phosphor layer, resulting in the subsequent emission of light. By varying the potential of the metal conductor 404 forming bridges 408 over the particle layer 402, the extent of this emission can be controlled.

As this structure is made smaller, the voltage required for emission is reduced such that useful currents should be obtained when potentials on the order of 100 volts are applied between particle layer 402 and the bridges 408. The points serve to smooth out irregularities in emission as well as increase the total emission available.

The structure in Figure 11 is fabricated as follows. First, a layer of encapsulated conductive metal particles, such as silver, is deposited on a silicon substrate 400 according to the method of the present invention. The resulting film is then crosslinked down to the substrate using an electron beam or another technique. An insulating layer of binder (or binder-encapsulated oxide particles) is then deposited, followed by deposition of another layer of encapsulated, conductive metal particles.

An electron beam with sufficient energy to crosslink the conductive and insulating layers down to the substrate is then directed to expose two parallel strips. A lower-energy electron beam is then used to expose two orthogonal
5 parallel strips such that only the upper conductive layer is crosslinked. This structure is then developed, and a surface layer of binder removed via argon-ion etching. This etching process exposes the points of the metal particles on the substrate 402 and the bridges 408,
10 forming the field emitter shown in Figure 11.

In this case, two conductive bridges 408 were provided, but any number of bridges may be constructed. A portion of the insulating support 406 and conductor 404 can be enlarged to provide a convenient contact pad 410
15 for electrical contact with the conductive bridge. Electrical contact with the substrate 400 can be made using known techniques.

Using the above techniques and the techniques for constructing overlapping interconnects, a field emitter
20 array can be fabricated in a fashion much like the thermal detector imaging array shown in Figure 2. The conductive bridge structures of the field emitter array differ structurally from their corresponding thermal detector components in that they are constructed as narrowly as
25 possible to minimize blockage of electron emission from the metal particle layer. The electrical interconnects differ in that only a single interconnect is required for each bridge. A single bridge structure or, alternately, a group of bridge structures can comprise each pixel.

30 Another application of space-charge-limited electrophoretic deposition is in the area of multilayer optical coatings. These coatings are composed of materials that prevent (or encourage) transmission of ultraviolet, visible, or infrared radiation. Suitable
35 selection of materials can provide passive control of radiation flow through glass.

Multilayer optical coatings typically have different

layers with different dielectric constants. The conventional method of making the multilayered structures is vacuum evaporation of the dielectric material. This process is far too expensive for mass producing coatings
5 on window glass, for example, due to the large number of layers needed, i.e., as many as 20 or more. However, the electrophoretic deposition method of the present invention permits depositing these materials without vacuum deposition on a mass production basis. The manufacturing
10 process is essentially mere xerography, i.e., the repeated electrophoretic deposition of particle layers comprised of appropriate pigments. Thick layers of glass can be used as a substrate by first corona charging the glass followed by electrophoresis. Such techniques for deposition are
15 well known in the xerographic art. Alternately, specific patterns can be exposed to form regions with differing indices of refraction. Applications include diffraction gratings.

Another application of space-charge-limited
20 electrophoretic deposition is in the elimination of semiconductor defects. Semiconductor components made from GaAs change state more rapidly than silicon, which is useful for binary logic applications such as a computer. One of the principle disadvantages of using GaAs as a
25 semiconductor material, however, is the tendency of the material to form dislocations. Dislocations are also a major limitation in the mass production of silicon and HgCdTe. J.B. Collige et al. in "Use of selective annealing for growing very large grain silicon on
30 insulator films" Appl. Phys. Lett. Vol. 41, No. 4, pp. 346-347 (Aug. 15, 1982), incorporated herein by reference, have demonstrated that a laser can preferentially melt a semiconductor in a region having patterns of material that half-wavelength match the laser light into the
35 semiconductor. For normal incidence, the deposited material should have an index of refraction approximately equal to the square root of the semiconductor's refractive

index and should have a thickness of a quarter wave. In "Natural Lithography" Appl. Phys. Lett. Vol. 41, No. 4, pp. 377-379 (Aug. 15, 1982), incorporated herein by reference, Deckman et al. demonstrated that a toner can be
5 preferentially electrophoretically deposited on dislocations or other imperfections on the surface of a semiconductor. Hence, if a particle layer comprised of particles having the proper index of refraction to half-wavelength match light into a semiconductor substrate is
10 deposited according to the present invention, laser annealing should preferentially melt only those regions of imperfection so as to eliminate the dislocations. Rapid thermal annealing, while solving some dislocation problems, typically creates others, such that it is
15 ineffective at curing dislocations in GaAs semiconductors. It is thought that lanthanum fluoride (LaF_3) would provide a sufficiently close match of dielectric constants to melt dislocations in gallium arsenide, although other materials could be substituted as well.

IN THE CLAIMS:

1. A method of forming a thermal detector imaging array having a plurality of elements, comprising the steps of:

1 electrophoretically depositing a first layer of toner
2 particles on a substrate, the first layer of toner
3 particles comprising a major amount of thermosensitive
4 particles encapsulated in a minor amount of thermoplastic
5 polymer binder that is insoluble in a low boiling point
6 aliphatic hydrocarbon liquid at ambient or room
7 temperatures and that is softenable at temperatures above
8 70°C, the binder having a plurality of functional sites
9 and having incorporated therein a minor amount of charge
10 director that is essentially nonconductive in aliphatic
11 hydrocarbon liquid in the absence of the binder;

12 crosslinking the first layer of toner particles in
13 predetermined areas corresponding to elements of the
14 thermal detector imaging array;

15 developing the first layer of toner particles;

16 electrophoretically depositing a second layer of
17 toner particles, the second layer of toner particles
18 comprising a major amount of conductive metal particles
19 encapsulated in a minor amount of thermoplastic polymer
20 binder that is insoluble in a low boiling point aliphatic
21 hydrocarbon liquid at ambient or room temperatures and
22 that is softenable at temperatures above 70°C, the binder
23 having a plurality of functional sites and having
24 incorporated therein a minor amount of charge director
25 that is essentially nonconductive in aliphatic hydrocarbon
26 liquid in the absence of the binder;

27 crosslinking the second layer of toner particles in
28 predetermined areas corresponding to a first pattern of
29 interconnects, the first pattern of interconnects being in
30 electrical contact with the crosslinked areas of the first
31 layer of toner particles at a first set of predetermined
32 contact locations;

33 developing the second layer of toner particles;

34 electrophoretically depositing a third layer of toner
35 particles, the third layer of toner particles comprising
36 a major amount of conductive metal particles encapsulated
37 in a minor amount of thermoplastic polymer binder that is
38 insoluble in a low boiling point aliphatic hydrocarbon
39 liquid at ambient or room temperatures and that is
40 softenable at temperatures above 70°C, the binder having
41 a plurality of functional sites and having incorporated
42 therein a minor amount of charge director that is
43 essentially nonconductive in aliphatic hydrocarbon liquid
44 in the absence of the binder;

45 crosslinking the third layer of toner particles in
46 predetermined areas corresponding to a second pattern of
47 interconnects that are orthogonal to the first pattern of
48 interconnects, the second pattern of interconnects being
49 in electrical contact with the crosslinked areas of the
50 first layer of toner particles at a second set of
51 predetermined contact locations; and

52 developing the third layer of toner particles.

1 2. The method of forming a thermal detector imaging
2 array as claimed in Claim 1, further comprising steps of:

3 electrophoretically depositing a fourth layer of
4 toner particles between the second and third layers of
5 toner particles, the fourth layer of toner particles
6 comprising a major amount of electrically insulating
7 particles encapsulated in a minor amount of thermoplastic
8 polymer binder that is insoluble in a low boiling point
9 aliphatic hydrocarbon liquid at ambient or room
10 temperatures and that is softenable at temperatures above
11 70°C, the binder having a plurality of functional sites
12 and having incorporated therein a minor amount of charge
13 director that is essentially nonconductive in aliphatic
14 hydrocarbon liquid in the absence of the binder;

15 crosslinking a predetermined pattern on the fourth
16 layer of toner particles at points of overlap of the first
17 and second patterns of interconnects; and

18 developing the fourth layer of toner particles.

1 3. The method of forming a thermal detector imaging
2 array as claimed in Claim 1, wherein the crosslinking step
3 is conducted using an electron beam.

1 4. The method of forming a thermal detector imaging
2 array as claimed in Claim 1, wherein the step of
3 crosslinking the first layer of toner particles comprises:
4 forming bridge supports at opposite ends of each
5 element by crosslinking a first portion of the first layer
6 of toner particles to a depth equal to the entire
7 thickness of the first layer of toner particles; and
8 for each element, forming bridge spans resting on and
9 extending between the bridge supports by crosslinking a
10 second portion of the first layer of toner particles to a
11 depth less than the entire thickness of the first layer of
12 toner particles.

1 5. The method of forming a thermal detector imaging
2 array as claimed in Claim 1, wherein the step of
3 crosslinking the third layer of toner particles comprises:
4 forming a plurality of conductive bridge spans
5 extending over the first pattern of interconnects at
6 points of overlap of the first and second patterns of
7 interconnects by crosslinking a first portion of the third
8 layer of toner particles to a depth less than the entire
9 thickness of the third layer of toner particles; and
10 forming a plurality of bridge supports beneath
11 opposite ends of the conductive bridge spans by
12 crosslinking a second portion of the third layer of toner
13 particles to a depth equal to the entire thickness of the
14 third layer of toner particles.

1 6. The method of forming a thermal detector imaging
2 array as claimed in Claim 1, wherein:
3 the step of depositing the first layer of toner

4 particles precedes the step of depositing the second layer
5 of toner particles; and
6 the step of depositing the second layer of toner
7 particles precedes the step of depositing the third layer
8 of toner particles.

1 7. The method of forming a thermal detector imaging
2 array as claimed in Claim 2, wherein:
3 the step of depositing the first layer of toner
4 particles precedes the step of depositing the second layer
5 of toner particles;
6 the step of depositing the second layer of toner
7 particles precedes the step of depositing the fourth layer
8 of toner particles; and
9 the step of depositing the fourth layer of toner
10 particles precedes the step of depositing the third layer
11 of toner particles.

1 8. A thermal detector imaging array, comprising:
2 a substrate;
3 a plurality of thermosensitive elements on the
4 substrate, the thermosensitive elements formed from a
5 first layer of toner particles comprising a major amount
6 of thermosensitive particles encapsulated in a minor
7 amount of thermoplastic polymer binder that is insoluble
8 in a low boiling point aliphatic hydrocarbon liquid at
9 ambient or room temperatures and that is softenable at
10 temperatures above 70°C, the binder having a plurality of
11 functional sites and having incorporated therein a minor
12 amount of charge director that is essentially
13 nonconductive in aliphatic hydrocarbon liquid in the
14 absence of the binder;
15 a first pattern of interconnects in electrical
16 contact with the thermosensitive elements at a first set
17 of predetermined contact locations, the first pattern of
18 interconnects being formed from a second layer of toner
19 particles comprising a major amount of conductive metal

20 particles encapsulated in a minor amount of thermoplastic
21 polymer binder that is insoluble in a low boiling point
22 aliphatic hydrocarbon liquid at ambient or room
23 temperatures and that is softenable at temperatures above
24 70°C, the binder having a plurality of functional sites
25 and having incorporated therein a minor amount of charge
26 director that is essentially nonconductive in aliphatic
27 hydrocarbon liquid in the absence of the binder; and
28 a second pattern of interconnects in electrical
29 contact with the thermosensitive elements at a second set
30 of predetermined contact locations, the second pattern of
31 interconnects being orthogonal to the first pattern of
32 interconnects and being formed from a third layer of toner
33 particles comprising a major amount of conductive metal
34 particles encapsulated in a minor amount of thermoplastic
35 polymer binder that is insoluble in a low boiling point
36 aliphatic hydrocarbon liquid at ambient or room
37 temperatures and that is softenable at temperatures above
38 70°C, the binder having a plurality of functional sites
39 and having incorporated therein a minor amount of charge
40 director that is essentially nonconductive in aliphatic
41 hydrocarbon liquid in the absence of the binder.

1 9. The thermal detector imaging array as claimed in
2 Claim 8, further comprising:
3 a plurality of insulating structures between the
4 first and second patterns of interconnects at the points
5 of overlap of the first and second patterns of
6 interconnects, the insulating structures formed from a
7 fourth layer of toner particles comprising a major amount
8 of electrically insulating particles encapsulated in a
9 minor amount of thermoplastic polymer binder that is
10 insoluble in a low boiling point aliphatic hydrocarbon
11 liquid at ambient or room temperatures and that is
12 softenable at temperatures above 70°C, the binder having
13 a plurality of functional sites and having incorporated
14 therein a minor amount of charge director that is

15 essentially nonconductive in aliphatic hydrocarbon liquid
16 in the absence of the binder.

1 10. The thermal detector imaging array as claimed in
2 Claim 8, wherein each of the plurality of thermosensitive
3 elements comprises a bridge span having a bridge support
4 beneath each end of the bridge span.

1 11. The thermal detector imaging array as claimed in
2 Claim 10, wherein the second pattern of interconnects
3 comprises a plurality of bridges that span the first
4 pattern of interconnects at the points of overlap of the
5 first and second patterns of interconnects.

1 12. The thermal detector imaging array as claimed in
2 Claim 8, wherein the substrate comprises a polymeric film
3 having a low heat capacity.

1 13. The thermal detector imaging array as claimed in
2 Claim 9, wherein the substrate comprises a polymeric film
3 having a low heat capacity.

1 14. The thermal detector imaging array as claimed in
2 Claim 8, wherein the thermosensitive particles comprise
3 metal particles covered with an oxide layer.

1 15. The thermal detector imaging array as claimed in
2 Claim 14, wherein the metal particles are selected from
3 the group consisting of copper, titanium and nickel.

1 16. The thermal detector imaging array as claimed in
2 Claim 15, wherein the metal particles are copper
3 particles.

1 17. A method of electrophoretic deposition,
2 comprising the steps of:
3 forming a toner by dry milling a major amount of

4 particles with an encapsulate comprising a thermoplastic
5 polymer binder that is insoluble in a low boiling
6 aliphatic hydrocarbon liquid at ambient or room
7 temperatures and that is softenable at temperatures above
8 70°C, the binder having a plurality of functional sites to
9 interact with a charge director;
10 comminuting the toner;
11 forming a suspension of toner particles by wet
12 milling the comminuted toner with a major amount of a low
13 boiling point aliphatic hydrocarbon liquid;
14 incorporating a charge director into the suspension,
15 the charge director being essentially nonconductive in the
16 absence of toner particles; and
17 depositing the toner particles from the suspension by
18 electrophoresis.

1 18. The method of electrophoretic deposition as
2 claimed in Claim 17, wherein the charge director is added
3 to the suspension after the wet milling.

1 19. The method of electrophoretic deposition as
2 claimed in Claim 17, wherein the charge director is added
3 to the comminuted toner during the wet milling.

1 20. The method as claimed in Claim 17, wherein the
2 encapsulated particles are deposited under space charge
3 limited current conditions.

1 21. The method of electrophoretic deposition as
2 claimed in Claim 17, wherein the dry milling is continued
3 for a period of time sufficient to obtain a uniform
4 distribution of the particles in the binder.

1 22. The method of electrophoretic deposition as
2 claimed in Claim 17, wherein the wet milling step is
3 continued for a period greater than 100 hours.

1 23. The method of electrophoretic deposition as
2 claimed in Claim 17, wherein the charge director is
3 selected from the group consisting of barium
4 sulfosuccinate and salts of bistridecyl sulfosuccinate.

1 24. The method of electrophoretic deposition as
2 claimed in Claim 17, wherein the particles are metals.

1 25. The method of electrophoretic deposition as
2 claimed in Claim 24, wherein the dry milling is conducted
3 under an atmosphere selected from the group consisting of
4 nitrogen and the noble gases.

1 26. The method of electrophoretic deposition as
2 claimed in Claim 24, wherein the metal particles are
3 selected from the group consisting of copper, nickel,
4 titanium and aluminum.

1 27. The method of electrophoretic deposition as
2 claimed in Claim 26, wherein the particles are copper.

1 28. The method of electrophoretic deposition as
2 claimed in Claim 24, wherein the particles are selected
3 from the group consisting of gold and silver.

1 29. The method of electrophoretic deposition as
2 claimed in Claim 17, further comprising the steps of:
3 exposing a charged photoconductive element with an
4 optical image of a predetermined pattern;
5 forming a corresponding toner particle pattern on the
6 photoconductive element by electrophoretically depositing
7 the toner particles from the suspension onto the
8 photoconductive element; and
9 transferring the toner particle pattern onto a
10 substrate.

1 30. The method of electrophoretic deposition as

2 claimed in Claim 24, further comprising the steps of:
3 exposing a charged photoconductive element with an
4 optical image of a predetermined pattern;
5 forming a corresponding toner particle pattern on the
6 photoconductive element by electrophoretically depositing
7 the toner particles from the suspension onto the
8 photoconductive element; and
9 transferring the toner particle pattern onto a
10 substrate.

1 31. The method of electrophoretic deposition as
2 claimed in Claim 30, wherein the substrate is an
3 electronic circuit board.

1 32. The method of electrophoretic deposition as
2 claimed in Claim 30, wherein photoconductive element is a
3 photoconductive drum and the substrate is a flexible
4 electronic circuit board.

1 33. The method of electrophoretic deposition as
2 claimed in Claim 30, wherein the pattern defines
3 interconnects on an integrated chip (IC).

1 34. The method of electrophoretic deposition as
2 claimed in Claim 33, wherein the pattern deposited on the
3 IC comprises lines with a width of less than five microns.

1 35. The method of electrophoretic deposition as
2 claimed in Claim 24, further comprising the step of
3 forming a thin layer of oxide on the metal particles.

1 36. The method of electrophoretic deposition as
2 claimed in Claim 35, wherein the deposited toner particles
3 have a small but finite resistance.

1 37. The method of electrophoretic deposition as
2 claimed in Claim 36, wherein the resistivity of the

3 deposited toner particles varies exponentially with
4 temperature.

1 38. The method of electrophoretic deposition as
2 claimed in Claim 37, wherein the metal particles are
3 selected from the group consisting of copper, nickel and
4 titanium.

1 39. The method of electrophoretic deposition as
2 claimed in Claim 17, wherein the particles are electrical
3 insulators.

1 40. The method of electrophoretic deposition as
2 claimed in Claim 24, wherein the metal particles are
3 partially oxidized to form electrical insulators.

1 41. The method of electrophoretic deposition as
2 claimed in Claim 24, wherein the metal particles are
3 completely oxidized.

1 42. The method of electrophoretic deposition as
2 claimed in Claim 40, wherein the metal particles are
3 selected from the group consisting of aluminum and
4 chromium.

1 43. A method of forming electrical interconnects on
2 an integrated chip (IC), comprising the steps of:
3 providing a semiconductor structure having a
4 plurality of elements requiring interconnects;
5 electrophoretically depositing a layer of toner
6 particles on the semiconductor structure, the layer of
7 toner particles having a major amount of conductive metal
8 particles and having a thermoplastic polymer binder that
9 is insoluble in a low boiling point aliphatic hydrocarbon
10 liquid at ambient or room temperatures and that is
11 softenable at temperatures above 70°C, the binder having
12 a plurality of functional sites and having incorporated

13 therein a minor amount of charge director that is
14 essentially nonconductive in aliphatic hydrocarbon liquid
15 in the absence of the binder;

16 crosslinking the layer of toner particles in
17 predetermined areas corresponding to a pattern of
18 interconnects in electrical contact with the elements
19 requiring interconnects; and

20 developing the layer of toner particles to remove the
21 toner particles from uncrosslinked areas.

1 44. The method of forming electrical interconnects
2 as claimed in Claim 43, further comprising repeatedly
3 performing the steps of:

4 electrophoretically depositing the layer of toner
5 particles;

6 crosslinking the layer of toner particles in
7 predetermined areas; and

8 developing the layer of toner particles.

1 45. The method of forming electrical interconnects
2 as claimed in Claim 43, wherein the crosslinking step is
3 conducted using an electron beam.

1 46. An integrated circuit (IC), comprising :

2 a semiconductor structure having a plurality of
3 elements requiring electrical connection; and

4 a pattern of interconnects in electrical contact with
5 the elements requiring electrical connection, the
6 interconnects comprising a layer of toner particles having
7 a major amount of conductive metal particles and a minor
8 amount of thermoplastic polymer binder that is insoluble
9 in a low boiling point aliphatic hydrocarbon liquid at
10 ambient or room temperatures and that is softenable at
11 temperatures above 70°C, the binder having a plurality of
12 functional sites and a minor amount of charge director
13 incorporated therein, the charge director being
14 essentially nonconductive in aliphatic hydrocarbon liquid

15 in the absence of toner particles.

1 47. An IC as claimed in Claim 46, wherein the first
2 pattern of interconnects bridges the second pattern of
3 interconnects at points of overlap of the first and second
4 pattern of interconnects.

1 48. An IC as claimed in Claim 46, further comprising
2 electrical connections between the interconnects and the
3 semiconductor structure.

1 49. A coating of particles electrophoretically
2 deposited under space-charge-limited current conditions,
3 the coating comprising:

4 a major amount of core particles;

5 a minor amount of thermoplastic polymer binder that
6 is insoluble in a low boiling aliphatic hydrocarbon liquid
7 at ambient or room temperatures and that is softenable at
8 temperatures above 70°C, the binder having a plurality of
9 functional sites; and

10 a minor amount of charge director incorporated into
11 the binder, the charge director being essentially
12 nonconductive in an aliphatic hydrocarbon liquid in the
13 absence of binder.

1 50. The coating of particles as claimed in Claim 49,
2 wherein the charge director is selected from the group
3 consisting of barium sulfosuccinate and salts of
4 bistridecyl sulfosuccinate.

1 51. The coating of particles as claimed in Claim 49,
2 wherein the core particles are metal particles.

1 52. The coating of particles as claimed in Claim 51,
2 wherein the metal particles are selected from the group
3 consisting of copper, nickel, titanium and aluminum.

1 53. The coating of particles as claimed in Claim 51,
2 wherein the metal particles are copper.

1 54. The coating of particles as claimed in Claim 51,
2 wherein the metal particles are selected from the group
3 consisting of gold and silver.

1 55. The coating of particles as claimed in Claim 51,
2 wherein the metal particles have a thin oxide layer.

1 56. The coating of particles as claimed in Claim 55,
2 wherein the resistivity of the coating varies
3 exponentially with temperature.

1 57. The coating of particles as claimed in Claim 56,
2 wherein the metal particles are selected from the group
3 consisting of copper, nickel and titanium.

1 58. The coating of particles as claimed in Claim 49,
2 wherein the core particles are electrical insulators.

1 59. The coating of particles as claimed in Claim 51,
2 wherein the metal particles are partially oxidized to form
3 electrical insulators.

1 60. The coating of particles as claimed in Claim 51,
2 wherein the metal particles are completely oxidized.

1 61. The coating of particles as claimed in Claim 59,
2 wherein the metal particles are selected from the group
3 consisting of aluminum and chromium.

1 62. A method of electron beam lithography,
2 comprising the steps of:
3 depositing on a substrate a layer of particles
4 encapsulated in a thermoplastic polymer binder having a
5 plurality of functional sites and a minor amount of charge

6 director incorporated therein;
7 forming bridge supports by crosslinking a first
8 portion of the layer of encapsulated particles with an
9 electron beam of sufficient energy to crosslink the layer
10 of encapsulated particles to a depth equal to the
11 thickness of the layer;
12 forming bridge spans resting on and extending between
13 the bridge supports by crosslinking a second portion of
14 the layer of encapsulated particles with an electron beam
15 of sufficient energy to crosslink the layer of
16 encapsulated particles to a depth less than the thickness
17 of the layer; and
18 removing portions of the layer of encapsulated
19 particles that have not been crosslinked.

1 63. The method of electron beam lithography as
2 claimed in Claim 62, further comprising forming the
3 encapsulated particles by the steps of:
4 dry milling a major amount of particles with an
5 encapsulate to form a toner, the encapsulate comprising a
6 thermoplastic binder having a plurality of functional
7 sites;
8 comminuting the toner;
9 wet milling the comminuted toner with a major amount
10 of a low boiling aliphatic hydrocarbon liquid to produce
11 a suspension of toner particles; and
12 incorporating a minor amount of charge director into
13 the suspension before depositing the toner particles from
14 the suspension on a substrate, the charge director being
15 essentially nonconductive in the absence of the toner
16 particles.

1 64. The method of electron beam lithography as
2 claimed in Claim 63, wherein the charge director is added
3 during the wet milling.

1 65. The method of electron beam lithography as

2 claimed in Claim 63, wherein the charge director is
3 selected from the group consisting of barium
4 sulfosuccinate and salts of bistridecyl sulfosuccinate.

1 66. A method of doping a semiconductor substrate,
2 comprising the steps of:
3 electrophoretically depositing from a suspension a
4 first layer of toner particles on the semiconductor
5 substrate, the toner particles having a major amount of
6 dopant particles and a minor amount of a thermoplastic
7 polymer binder that is insoluble in a low boiling point
8 aliphatic hydrocarbon liquid at ambient or room
9 temperatures and that is softenable at temperatures above
10 70°C, the binder having a plurality of functional sites
11 and a minor amount of charge director incorporated
12 therein;
13 crosslinking the layer of toner particles in areas
14 where doping is desired;
15 developing the layer of toner particles to remove the
16 toner particles that have not been crosslinked; and
17 heating the substrate to drive off the binder and
18 diffuse the dopant particles into the substrate.

1 67. The method of doping a semiconductor substrate
2 as claimed in Claim 66, wherein the charge director is
3 essentially nonconductive in aliphatic hydrocarbon liquid
4 in the absence of the toner particles.

1 68. A method of forming micrometallic structures,
2 comprising the steps of:
3 electrophoretically depositing on a substrate a
4 layer of toner particles having a major amount of
5 conductive metal particles and a minor amount of
6 thermoplastic polymer binder that is insoluble in a low
7 boiling point aliphatic hydrocarbon liquid at ambient or
8 room temperatures and that is softenable at temperatures
9 above 70°C, the binder having a plurality of functional

10 sites and having incorporated therein a minor amount of
11 charge director that is essentially nonconductive in
12 aliphatic hydrocarbon liquid in the absence of the binder;
13 crosslinking at least a first portion of the layer of
14 toner particles throughout the entire thickness of the
15 layer of toner particles to form a plurality of support
16 structures; and

17 crosslinking at least a second portion of the layer
18 of toner particles to a depth less than the entire
19 thickness of the layer of toner particles to form a
20 plurality of suspended structures contiguous with the
21 support structures, each suspended structure being
22 supported by at least one support structure;

23 developing the layer of toner particles to remove the
24 toner particles that have not been crosslinked; and

25 heating the first and second crosslinked portions to
26 evaporate the binder and fuse the metal particles.

1 69. The method of forming micrometallic structures
2 as claimed in Claim 68, wherein the crosslinking step is
3 accomplished by using an electron beam.

1 70. A method of forming a field emitter, comprising
2 the steps of:

3 electrophoretically depositing a first layer of toner
4 particles having a thermoplastic polymer binder insoluble
5 in a low boiling point aliphatic hydrocarbon liquid at
6 ambient or room temperatures and that is softenable at
7 temperatures above 70°C, the binder having a plurality of
8 functional sites and a minor amount of charge director
9 incorporated therein, the first layer of toner particles
10 having a major amount of conductive metal particles;

11 crosslinking a predetermined pattern on the first
12 layer of toner particles;

13 electrophoretically depositing a second layer of
14 toner particles having a thermoplastic polymer binder that
15 is insoluble in a low boiling point aliphatic hydrocarbon

16 liquid at ambient or room temperatures and that is
17 softenable at temperatures above 70°C, the binder having
18 a plurality of functional sites and a minor amount of
19 charge director incorporated therein;

20 crosslinking a predetermined pattern on the second
21 layer of toner particles to form at least one insulating
22 support;

23 electrophoretically depositing a third layer of toner
24 particles having thermoplastic polymer binder that is
25 insoluble in a low boiling point aliphatic hydrocarbon
26 liquid at ambient or room temperatures and that is
27 softenable at temperatures above 70°C, the binder having
28 a plurality of functional sites and a minor amount of
29 charge director incorporated therein, the second layer of
30 toner particles having a major amount of the conductive
31 metal particles;

32 crosslinking a predetermined pattern on the third
33 layer of toner particles to form at least one metal
34 structure having a first portion suspended over a region
35 of the pattern crosslinked on first layer of toner
36 particles and a second portion resting on the insulating
37 support;

38 developing the layers of toner particles to remove
39 uncrosslinked portions; and

40 etching the resulting device to partially expose the
41 metal particles in the first and third layers of toner
42 particles.

1 71. The method of forming a field emitter as claimed
2 in Claim 70, wherein the charge director is essentially
3 nonconductive in aliphatic hydrocarbon liquid in the
4 absence of the toner particles.

1 72. The method of forming a field emitter as claimed
2 in Claim 71, wherein the second layer of toner particles
3 contains a major amount of electrically insulating
4 particles.

1 73. The method of forming a field emitter as claimed
2 in Claim 71, wherein the etching step is conducted using
3 argon-ion etching.

1 74. The method of forming a field emitter as claimed
2 in Claim 71, wherein the first, second, and third
3 crosslinking steps are conducted using an electron beam.

1 75. The method of forming a field emitter as claimed
2 in Claim 74, wherein the steps of crosslinking the second
3 and third layers are combined into a single step
4 comprising:

5 crosslinking a predetermined pattern extending
6 throughout the second and third layers of toner particles
7 to form the insulating support and the resting portion of
8 the metal structure; and

9 crosslinking an additional predetermined pattern
10 extending throughout the third layer of toner particles to
11 form the suspended portion of the metal structure.

1 76. A field emitter, comprising:

2 a first layer of toner particles having a
3 multiplicity of exposed metallic points for electron
4 emission, the first layer of toner particles having a
5 major amount of conductive metal particles and a
6 thermoplastic polymer binder that is insoluble in a low
7 boiling point aliphatic hydrocarbon liquid at ambient or
8 room temperatures and that is softenable at temperatures
9 above 70°C, the binder having a plurality of functional
10 sites and a minor amount of charge director incorporated
11 therein;

12 a second layer of toner particles forming at least
13 one insulating structure resting on the first layer of
14 toner particles, the second layer of toner particles
15 having a thermoplastic polymer binder that is insoluble in
16 a low boiling point aliphatic hydrocarbon liquid at
17 ambient or room temperatures and that is softenable at

18 temperatures above 70°C, the binder having a plurality of
19 functional sites and a minor amount of charge director
20 incorporated therein; and

21 a third layer of toner particles forming at least one
22 bridge structure having a first portion resting on and
23 supported by the insulating structures and a second
24 portion extending over the metallic points, the third
25 layer of toner particles having a major amount of
26 conductive metal particles and a thermoplastic polymer
27 binder that is insoluble in a low boiling point aliphatic
28 hydrocarbon liquid at ambient or room temperatures and
29 that is softenable at temperatures above 70°C, the binder
30 having a plurality of functional sites and a minor amount
31 of charge director incorporated therein.

1 77. The field emitter claimed in Claim 76, wherein
2 the second layer of toner particles further comprises a
3 major amount of electrically insulating particles.

1 78. The field emitter claimed in Claim 76, wherein
2 the second layer of toner particles further comprises a
3 major amount of metal particles having an electrically
4 insulating oxide layer.

1 79. A method of forming an optical coating
2 comprising the steps of:
3 electrophoretically depositing on an optical
4 substrate a layer of toner particles, the layer of toner
5 particles comprising a major amount of electromagnetic-
6 radiation-influencing particles encapsulated in a minor
7 amount of thermoplastic polymer binder that is insoluble
8 in a low boiling point aliphatic hydrocarbon liquid at
9 ambient or room temperatures and that is softenable at
10 temperatures above 70°C, the binder having a plurality of
11 functional sites and having incorporated therein a minor
12 amount of charge director that is essentially
13 nonconductive in aliphatic hydrocarbon liquid in the

14 absence of the binder;
15 crosslinking the layer of toner particles in a
16 predetermined pattern; and
17 developing the layer toner particles to remove toner
18 particles that have not been crosslinked.

1 80. The method of forming an optical coating as
2 claimed in Claim 79, wherein the electromagnetic-
3 radiation-influencing particles are selected from the
4 group consisting of lanthanum fluoride and calcium
5 fluoride.

1 81. The method of forming an optical coating as
2 claimed in Claim 79, further comprising heating the layer
3 of toner particles to drive off the binder.

1 82. The method of forming an optical coating as
2 claimed in Claim 79, further comprising corona charging
3 the substrate prior to the electrophoretic deposition
4 step.

1 83. The method of forming an optical coating as
2 claimed in Claim 82, wherein the substrate is glass.

1 84. An optical coating comprising:
2 a layer of toner particles in a predetermined
3 pattern, the layer of toner particles comprising a major
4 amount of electromagnetic-radiation-influencing particles
5 encapsulated in a minor amount of thermoplastic polymer
6 binder that is insoluble in a low boiling point aliphatic
7 hydrocarbon liquid at ambient or room temperatures and
8 that is softenable at temperatures above 70°C, the binder
9 having a plurality of functional sites and a minor amount
10 of charge director incorporated therein.

1 85. The optical coating as claimed in Claim 84,
2 wherein the electromagnetic-radiation-influencing

3 particles are selected from the group consisting of
4 lanthanum fluoride and calcium fluoride.

1 86. The optical coating as claimed in Claim 84,
2 wherein the predetermined pattern is a diffraction
3 grating.

1 87. A method of selectively curing semiconductor
2 dislocations comprising the steps of:
3 selectively electrophoretically depositing a layer of
4 toner particles on a semiconductor substrate, the layer of
5 toner particles comprising a major amount of core
6 particles encapsulated in a minor amount of thermoplastic
7 polymer binder that is insoluble in a low boiling point
8 aliphatic hydrocarbon liquid at ambient or room
9 temperatures and that is softenable at temperatures above
10 70°C, the binder having a plurality of functional sites
11 and having incorporated therein a minor amount of charge
12 director that is essentially nonconductive in aliphatic
13 hydrocarbon liquid in the absence of the binder, the layer
14 of toner particles having a predetermined refractive index
15 and thickness; and
16 exposing the layer of toner particles to
17 electromagnetic radiation of a predetermined wavelength.

1 88. The method of selectively curing semiconductor
2 dislocations as claimed in Claim 87, wherein the layer of
3 toner particles has a refractive index approximately equal
4 to the square root of the refractive index of the
5 semiconductor and has a thickness of approximately one
6 quarter of the radiation wavelength.

1 89. The method of selectively curing semiconductor
2 dislocations as claimed in Claim 88 wherein the exposing
3 step is conducted using laser irradiation.

1 90. The method of selectively curing semiconductor

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2 dislocations as claimed in Claim 88, wherein the
3 semiconductor is gallium arsenide and the core particles
4 are lanthanum fluoride.

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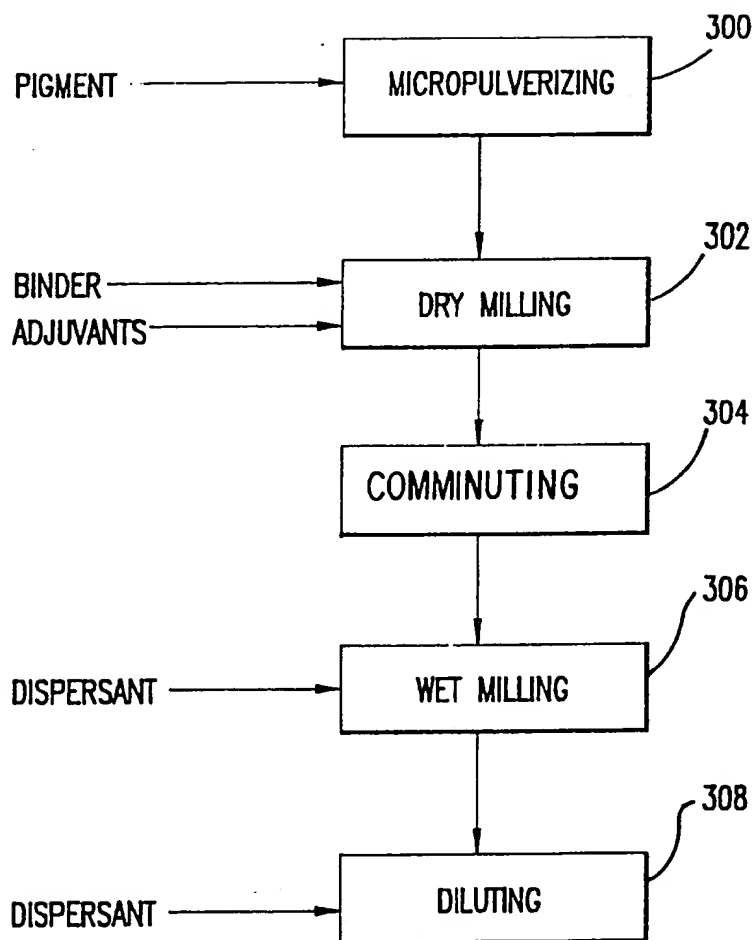


FIG.1

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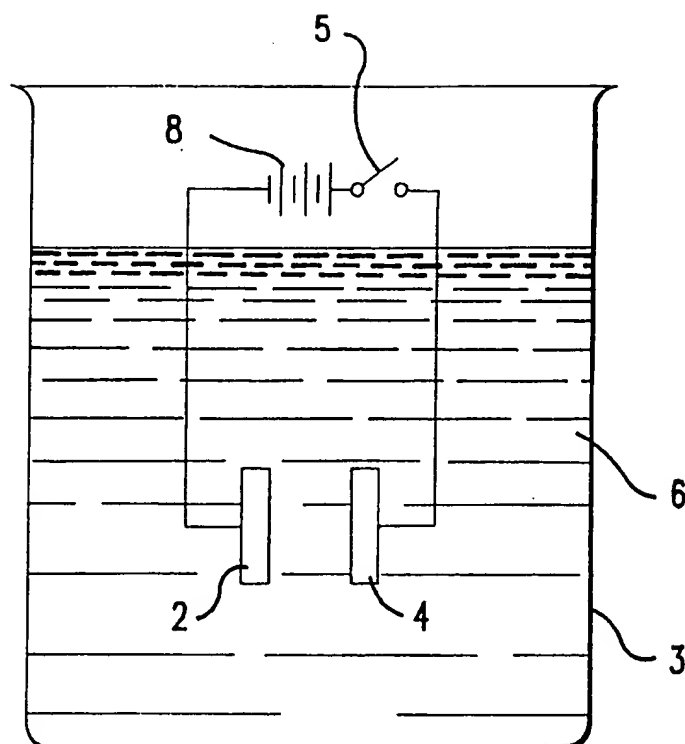


FIG.1A

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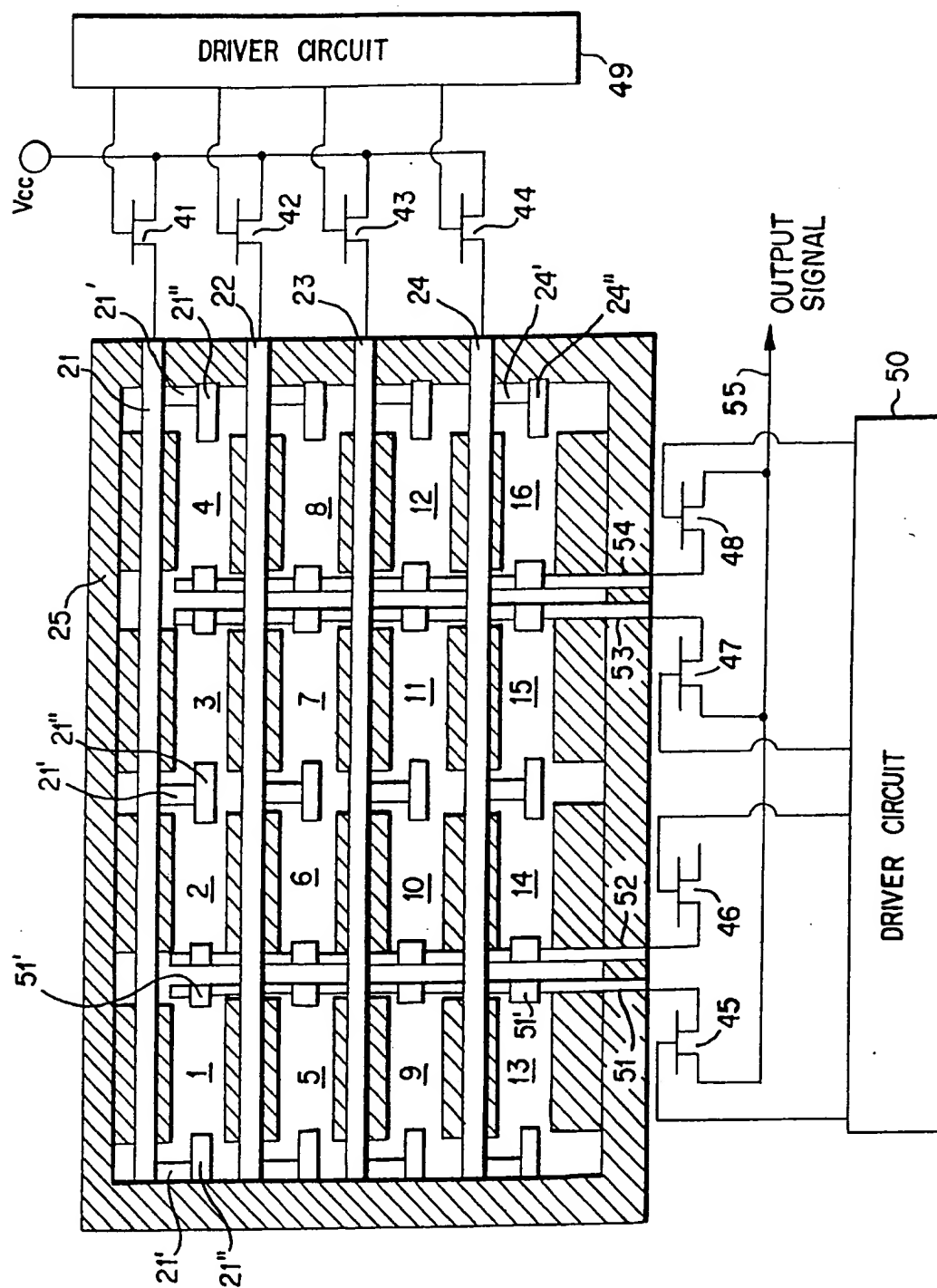


FIG. 2

SUBSTITUTE SHEET

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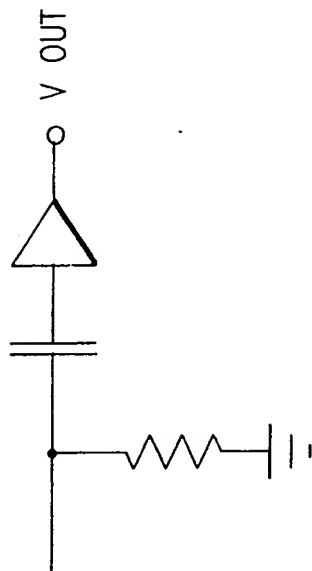


FIG. 3B

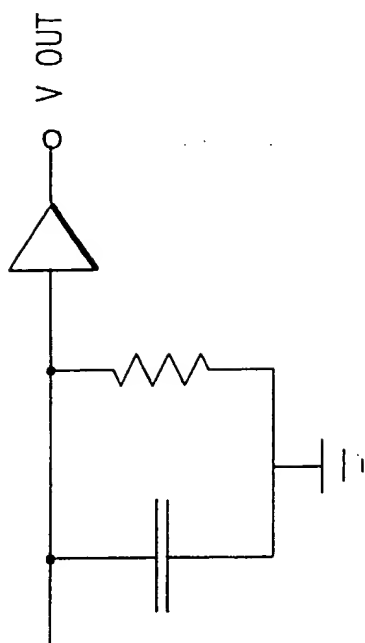


FIG. 3A

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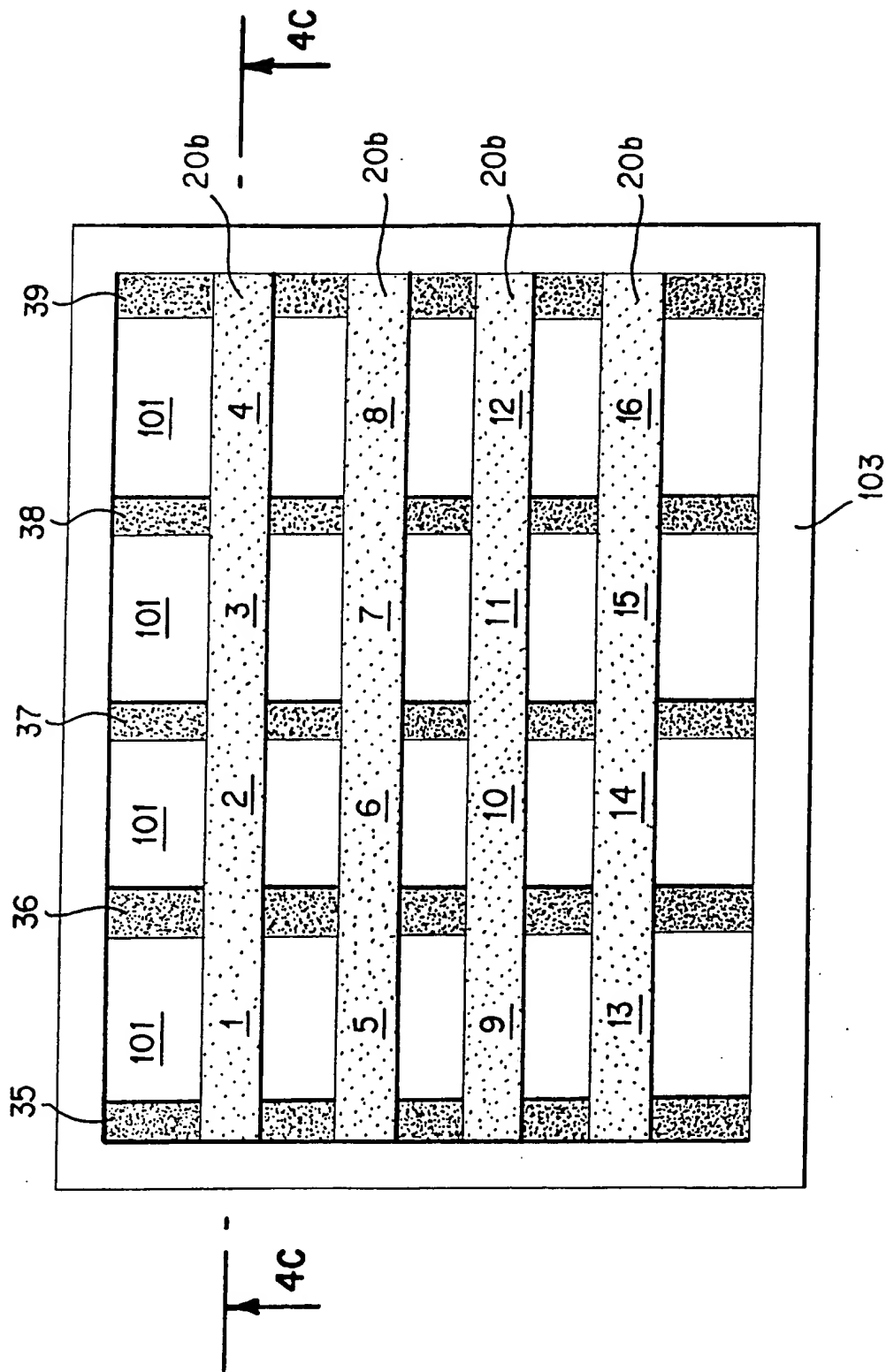


FIG. 4

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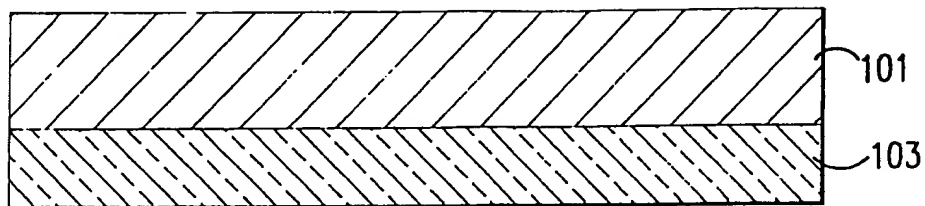


FIG.4A

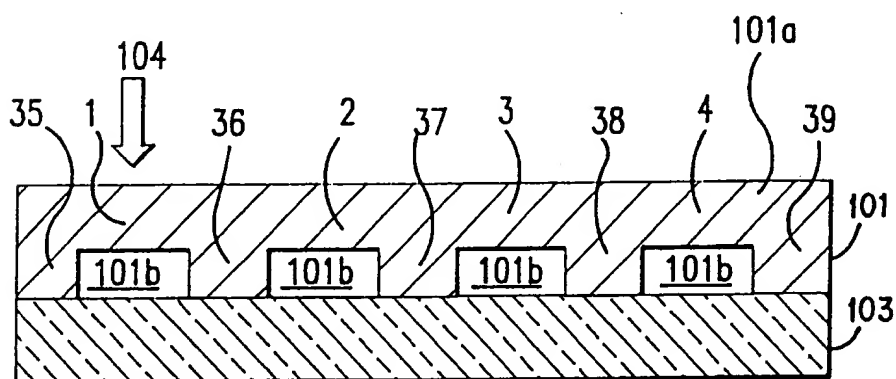


FIG.4B

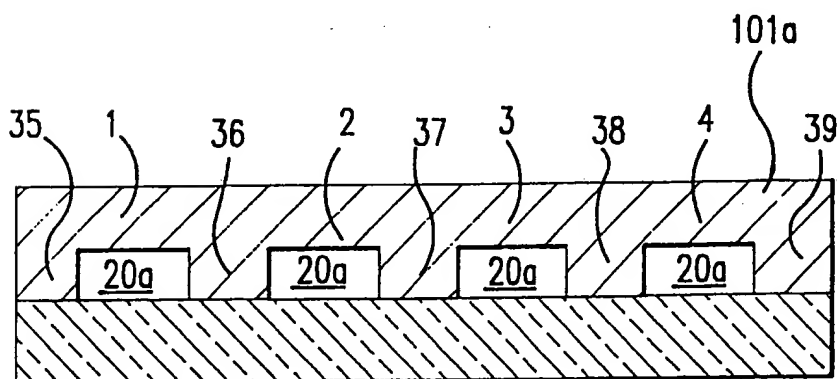
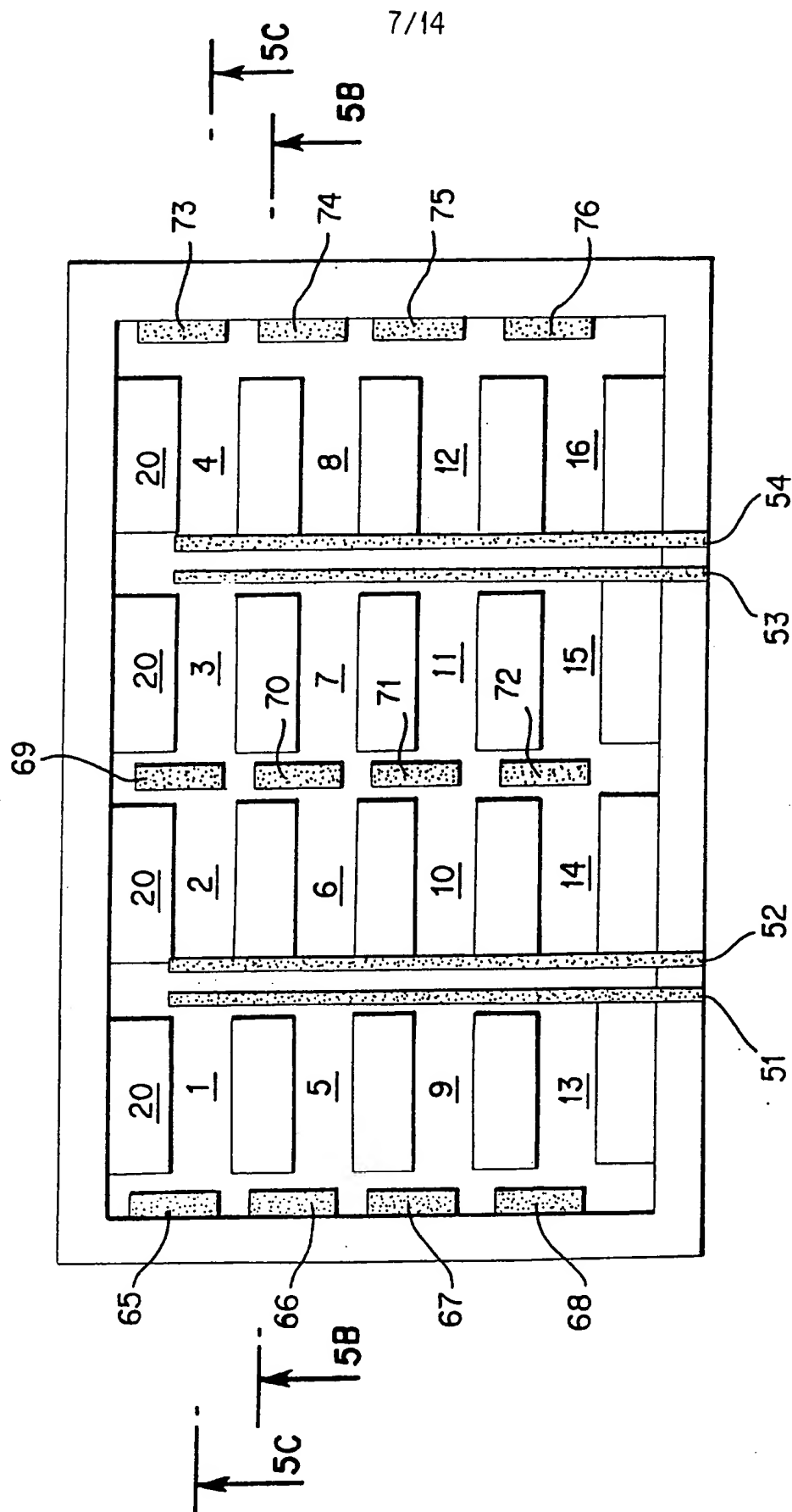


FIG.4C



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FIG.5B

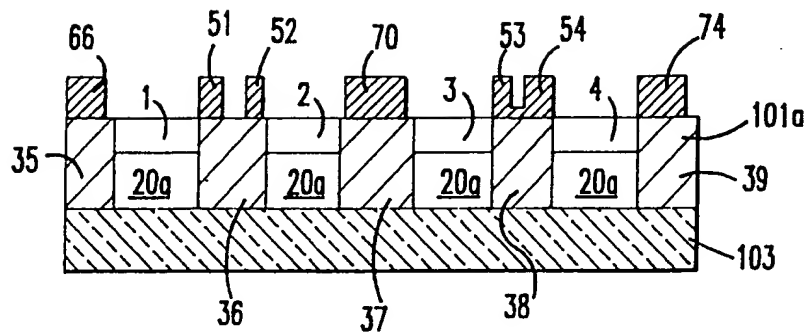


FIG.5C

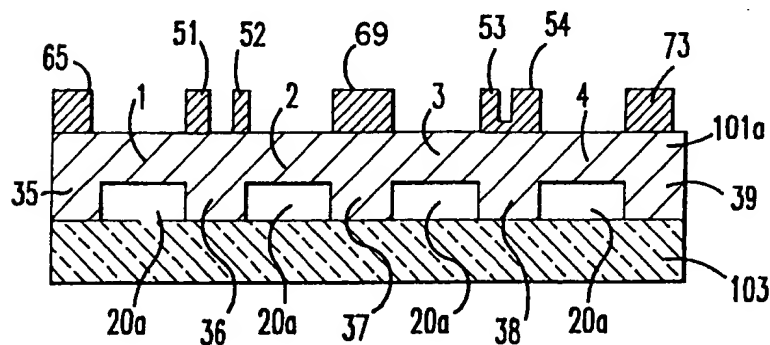


FIG.6B

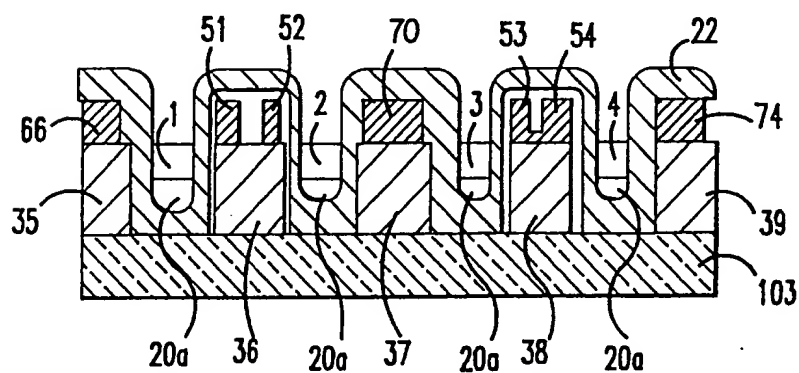
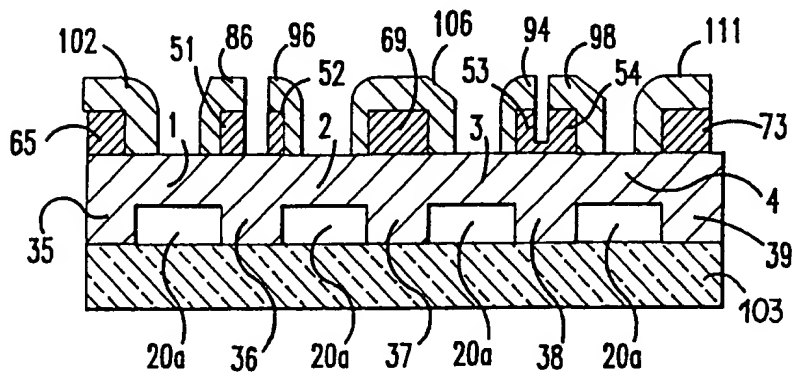


FIG.6C



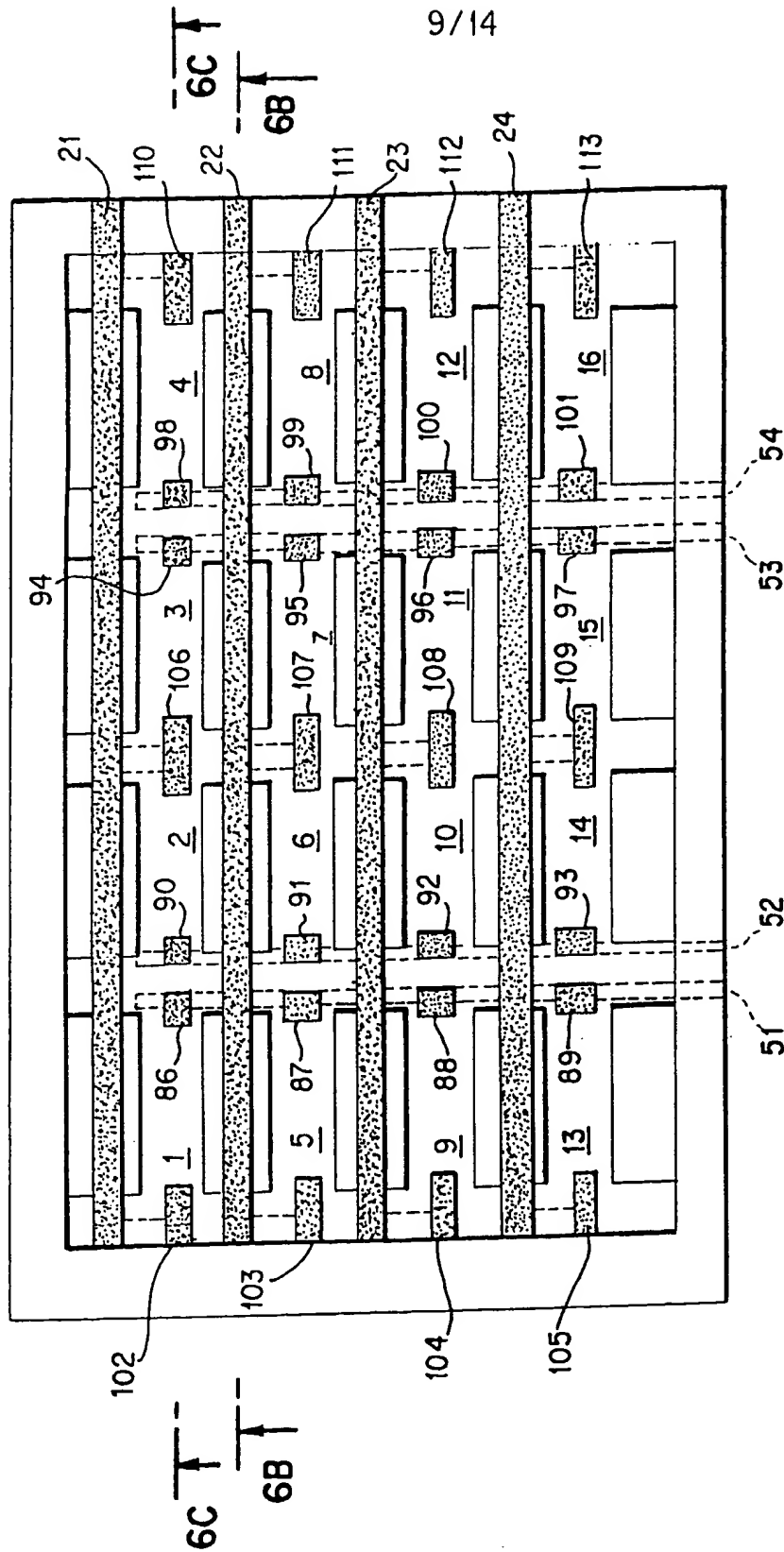


FIG. 6A

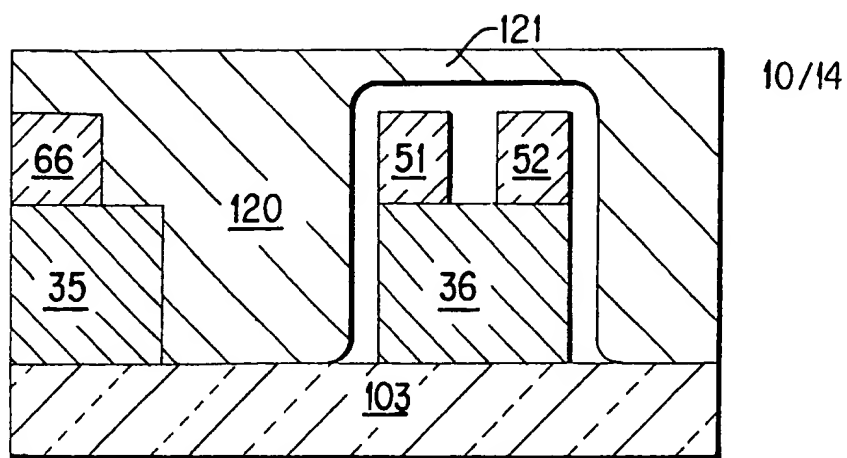


FIG. 7A

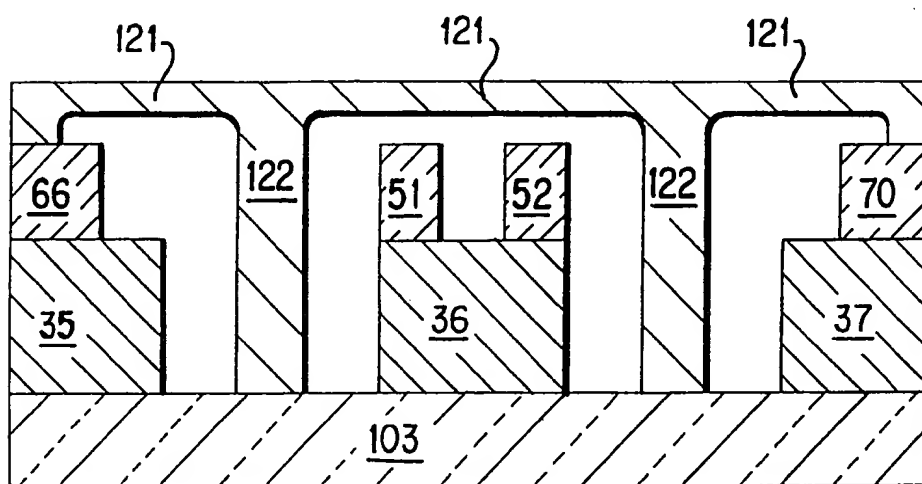


FIG. 7B

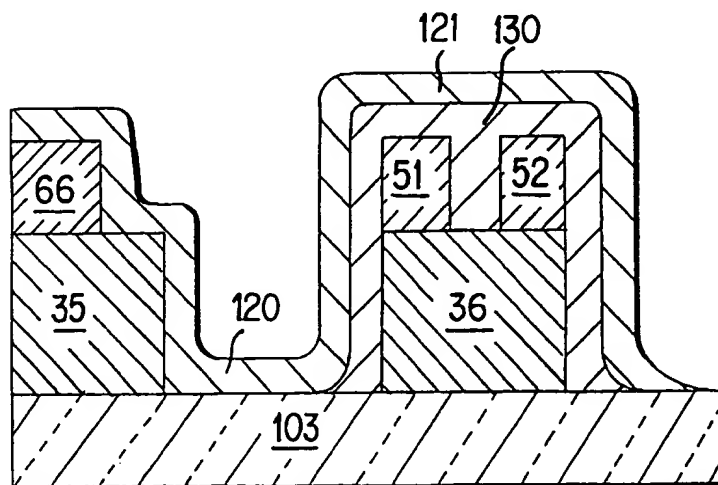


FIG. 7C

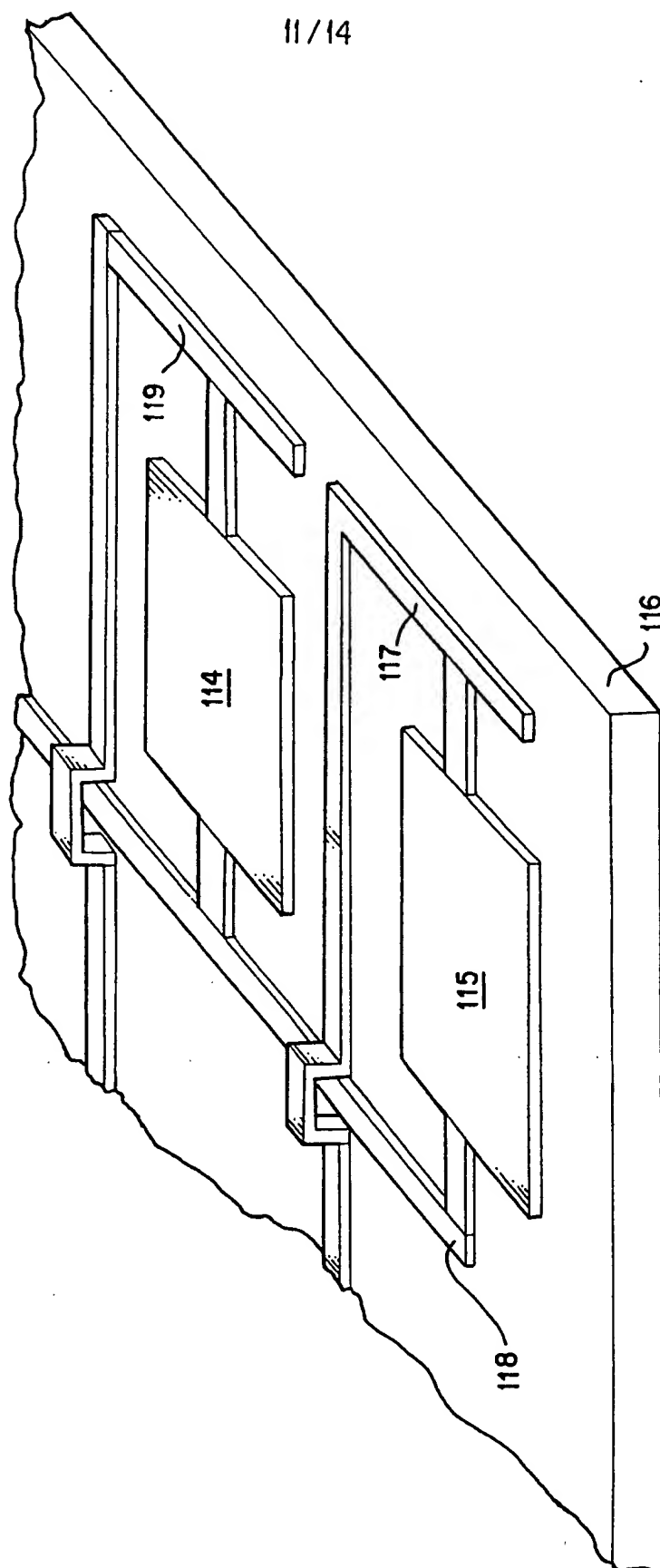


FIG. 8

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FIG.9A

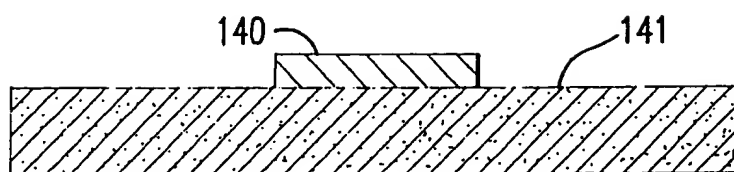


FIG.9B

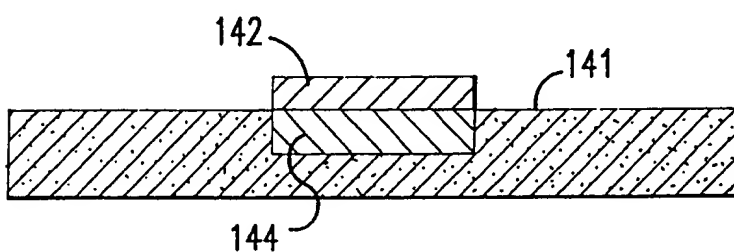


FIG.9C

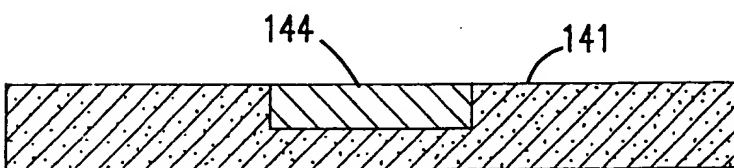


FIG.9D

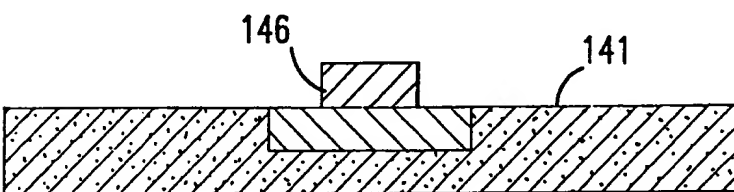
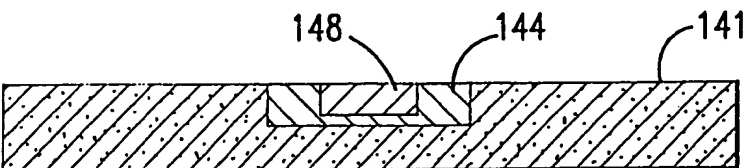


FIG.9E



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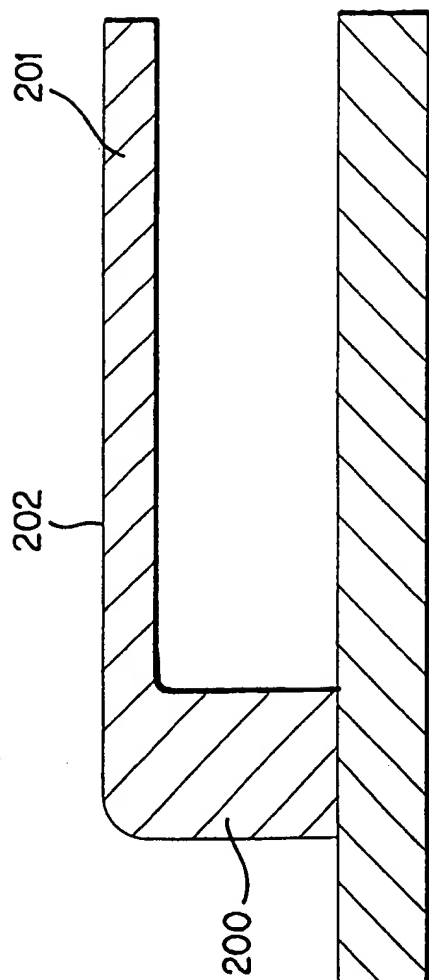


FIG. 10

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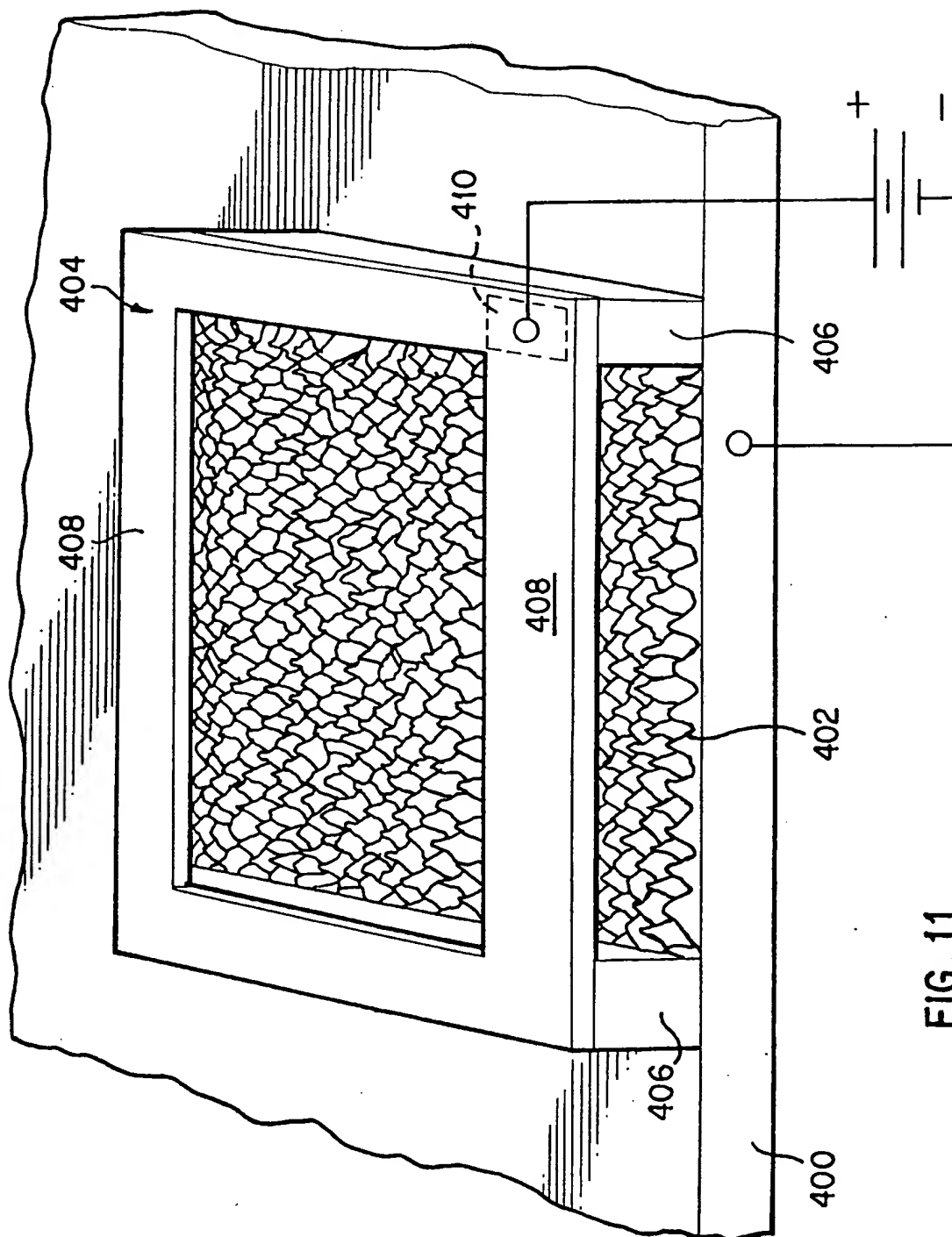


FIG. 11